

## ACKNOWLEDMENTS

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## ABSTRACT

The purpose of this research was to evaluate the effects of adding Procter and Gamble calcium carbonate seed crystals during water softening by chemical precipitation. The Procter and Gamble seed crystals were originally designed to improve the effectiveness of detergents. Heterogeneous nucleation, or the presence of nucleating agents such as seed crystals, lowers the free energy of crystallization in comparison to the absence of nucleating surfaces, or homogeneous nucleation. Heterogeneous nucleation can also increase the size of the precipitate, allowing it to settle more effectively from solution.

Synthetic and real hard waters were used to explore the effects of adding seed crystals when softening by the addition of lime ( $\text{CaO}$ ) or caustic soda ( $\text{NaOH}$ ). The seed crystals used in these experiments were reagent-grade calcium carbonate, calcium carbonate prepared by a proprietary process of Procter and Gamble, and the dried softening sludge solids from two municipal water treatment facilities.

On the basis of specific surface area, there was no significant difference between the performances of the Procter and Gamble seed and the reagent-grade calcite in removing calcium hardness, while the performance of the dried sludge solids differed between locations. In tests with real waters, the presence of seed crystals helped to increase the precipitation of calcium carbonate when softening with caustic soda. Natural organic matter appeared to inhibit the precipitation and removal of calcium from synthetic hard water during heterogeneous nucleation, but had no significant effect on the softening of real waters.

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## CHAPTER 1: INTRODUCTION

This study evolved from the work of Procter and Gamble to explore the effects of adding crushed calcium carbonate crystals to their detergents in order to improve their effectiveness. During the laundering process, calcium and magnesium ions in hard water interfere with surfactants (surface active agents) in detergents, inhibiting their ability to remove dirt and stains from fabrics. In addition, the deposition of minerals, notably calcium carbonate, in the water turns clothes gray and leaves them feeling stiff. Formerly, phosphate builders in detergents were used to bind hardness minerals and hold them in solution until they could be rinsed away. However, the Clean Detergent Act of 1987, seeking to reduce the amount of phosphorus in rivers, lakes and estuaries, prohibits the use of detergents containing phosphorus (phosphates).

The aim of Procter and Gamble's research was to develop very fine seed crystals that could pass through the fabric of clothing yet still remove the hardness in the water by chemical precipitation onto the seed crystals. However, testing by Procter and Gamble showed that the detergent surfactants adsorbed to the seed crystal surfaces, "poisoning" crystal growth and inhibiting the removal of calcium hardness. In light of this, other uses for these calcium carbonate seed crystals were explored, and the question arose as to whether these seed crystals could be effectively employed by water utilities to assist in the softening of drinking water.

This study evaluated the effectiveness of adding seed crystals of calcite (calcium carbonate), specifically the Procter and Gamble seed crystals, during water softening by

chemical precipitation. Calcium carbonate precipitation results in a reduction of dissolved calcium, while overall calcium removal is achieved both by precipitation of the dissolved calcium and by subsequent settling of the calcium carbonate precipitate. This process is called homogenous nucleation if it takes place in the absence of surfaces that can assist in nucleation. If nucleating agents such as seed crystals are present, this process is known as heterogeneous nucleation. In the absence of other available surfaces, the presence of seed crystals of calcium carbonate should increase the rate of precipitation of calcium carbonate by lowering the free energy of crystallization, in addition to increasing the size of the precipitate and its ability to settle effectively from solution. The seed crystals chosen for this study included the Procter and Gamble seed crystals, reagent-grade calcium carbonate crystals, and dried sludge solids collected from two water softening treatment plants.

In order to evaluate the effectiveness of the Procter and Gamble seed crystals on the precipitative softening of hard waters, experiments with and without seed crystals (heterogeneous and homogenous precipitation, respectively) were conducted on a model water with and without natural organic matter (NOM), and on two real hard waters, one with low total organic carbon (TOC) and one with high TOC. These experiments were conducted with two bases typically employed in water softening, caustic soda (NaOH), and more commonly, lime (CaO). The results of homogenous precipitation were compared with the heterogeneous precipitation achieved through the addition of the Procter and Gamble seed crystals, and these results were then compared with those achieved by the other seed crystals.

## CHAPTER 2: BACKGROUND AND THEORETICAL CONSIDERATIONS

### 2.1 Hard Water

Water hardness is defined as the sum of all polyvalent cations present in water [1]. For most natural waters, hardness is due primarily to calcium and magnesium. The sum of these two ions is referred to as the total hardness of a water and is commonly expressed in units of mg/L as  $\text{CaCO}_3$ . Water hardness can be generally classified according to the specifications in Table 2.1, and a common water treatment goal is to provide water with a total hardness in the range of 75 to 120 mg/L as  $\text{CaCO}_3$  [2].

Table 2.1

Hard Water Classification

Hardness Range (mg/L as $\text{CaCO}_3$ )	Description
0-75	Soft
75-100	Moderately Hard
100-300	Hard
>300	Very Hard

Source: Cornwell, 1998

Hard water is undesirable for several reasons. Aesthetically, hard water does not lather well and leaves a residue on clothing and bathtubs. This scum is a result of the reactions between calcium and magnesium with soap, described by Equation 2-1 [2].



In addition to leaving undesirable precipitates, this complexation reaction inhibits soap from interacting with dirt and stains on clothing, hindering the laundering process.

The other major problem with hard water is that it produces scale in hot water pipes and heaters. This scale is often a hard, white deposit composed mostly of calcium carbonate in the form of calcite. The formation of scale can be described by



When this lime scale forms, it constricts and clogs pipes and can damage water-using appliances (e.g., washing machines, dishwashers, and water heaters). Scale also reduces thermal efficiency because it insulates water from heating elements, requiring the use of more energy in both industrial and domestic situations.

Water hardness is primarily a function of the geology of the area from where the water is drawn. Waters underlain by limestone are prone to hard water because rainfall continually dissolves the rock and carries the dissolved cations to the water system [3].

In the United States, hard water is prevalent wherever there are limestone deposits.

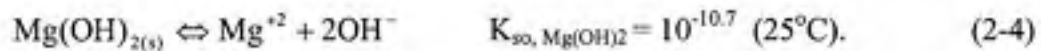
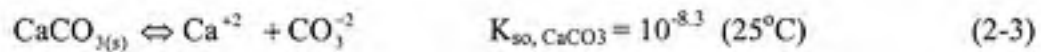
In order to alleviate these problems, water is softened (i.e. calcium and magnesium ions are removed). Softening water has other benefits in addition to calcium and magnesium removal, including the removal of other undesirable dissolved impurities such as radium, heavy metals, certain organic compounds, silica, fluoride, iron, and manganese [4]. The degree of removal of these species depends on the treatment processes used and the original water characteristics.



## 2.2 Precipitative Softening

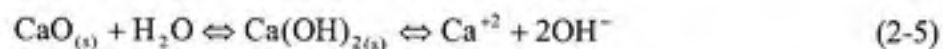
### 2.2.1 Solubility Considerations

Several water treatment processes can remove hardness, including ion exchange, membrane separation, and chemical precipitation. Chemical precipitation, the most widely used softening treatment and the focus of this study, involves raising the pH of the water so that the solubilities of calcium carbonate ( $\text{CaCO}_{3(s)}$ ) and magnesium hydroxide ( $\text{Mg}(\text{OH})_{2(s)}$ ) are both exceeded. The solubility expressions and solubility constants for these two solids are given as follows [5]:



Exceeding the solubility of these solids is achieved through addition of a base such as caustic soda ( $\text{NaOH}$ ), soda ash ( $\text{Na}_2\text{CO}_3$ ), or most commonly lime ( $\text{CaO}$ ). With the rise in pH that accompanies an addition of base, bicarbonate is converted into carbonate, and the calcium carbonate solubility described in Equations 2.2 and 2.3 is exceeded. The pH must be raised to around 10.8 before magnesium hydroxide will noticeably precipitate [6].

Currently more than 1000 water plants in the United States use lime softening processes, with a majority of these found in the Midwestern states and Florida [4]. Lime or quicklime ( $\text{CaO}$ ) is the largest tonnage chemical used in the treatment of potable and industrial water supplies [7]. Water is added to "slake" the lime, resulting in a suspension of  $\text{Ca}(\text{OH})_2$  or "milk of lime":

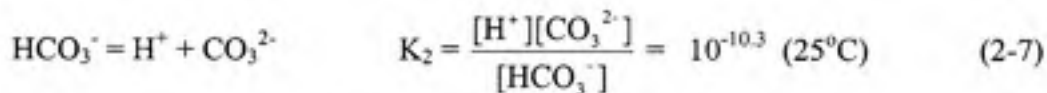
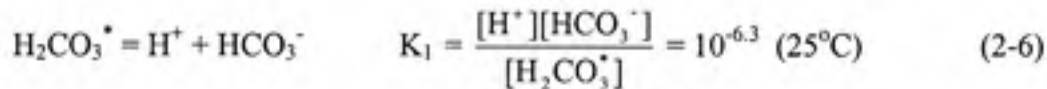


Although calcium hydroxide becomes a source of calcium hardness, this added calcium is precipitated as  $\text{CaCO}_{3(s)}$  because the hydroxide raises the pH of the treated water. When

the carbonate is exhausted, further lime addition will only serve to increase the calcium hardness. This creates an optimum lime dose that should not be exceeded without the subsequent addition of more carbonate, which is accomplished by the addition of soda ash ( $\text{Na}_2\text{CO}_3$ ); this procedure is termed lime-soda softening. Similar to lime softening, softening with caustic soda or soda ash raises the pH, except that there is no addition of calcium hardness. Again, carbonate must be present in a stoichiometric quantity for effective hardness removal.

### 2.2.2 Carbonate Chemistry

The carbonate system plays a significant role in the chemistry of precipitative softening, both in terms of buffering and in providing the carbonate necessary for calcium removal. Defining  $\text{H}_2\text{CO}_3^*$  as the sum of dissolved  $\text{CO}_2$  and  $\text{H}_2\text{CO}_3$  leads to the following speciation and corresponding equilibrium constants [5]:



Defining the total carbonic acid species concentration as  $C_T$  gives:

$$C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (2-8)$$

The distribution of the various carbonic acid species can be expressed by their specific ionization fractions ( $\alpha$ ) as follows:

$$\alpha_0 = \frac{[\text{H}_2\text{CO}_3^*]}{C_T} = \frac{1}{1 + K_1/[\text{H}^+] + K_1K_2/[\text{H}^+]^2} \quad (2-9)$$

$$\alpha_1 = \frac{[\text{HCO}_3^-]}{C_T} = \frac{1}{[\text{H}^+]/K_1 + 1 + K_2/[\text{H}^+]} \quad (2-10)$$

$$\alpha_2 = \frac{[\text{CO}_3^{2-}]}{C_T} = \frac{1}{[\text{H}^+]^2 / (K_1 K_2) + [\text{H}^+] / K_2 + 1} \quad (2-11)$$

### 2.2.3 Charge Balance Considerations

A charge balance for the solution must be maintained in order to preserve overall system electroneutrality. The charge balance for the major constituents considered in water softening should take the form

$$2[\text{Ca}^{+2}] + 2[\text{Mg}^{+2}] + [\text{H}^+] + C_B = C_T(\alpha_1 + 2\alpha_2) + [\text{OH}^-] + C_A \quad (2-12)$$

where  $\alpha_1 C_T$  and  $2\alpha_2 C_T$  represent  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , respectively, and  $C_B$  and  $C_A$  account for any other charged species (positive and negative, respectively) that are not explicitly listed. Depending on the source water,  $C_B$  should consist mostly of sodium, potassium, and iron, while  $C_A$  would most probably consist of chloride and sulfate. The units of  $C_A$  and  $C_B$  are equivalents per liter

The charge balance is a critical component of a precipitative softening equilibrium model. As previously mentioned, the addition of lime increases the calcium ion concentration, which must be accounted for in the charge balance. Caustic soda and soda ash additions will both affect  $C_B$ ; soda ash addition also contributes to the  $C_T$  of the system.

### 2.2.4 Modeling Precipitative Softening

In order to model precipitative softening, certain assumptions must be made. The first assumption is that the system is closed, meaning there is no  $\text{CO}_2$  exchange with the atmosphere to affect the carbonate content of the water. This is a reasonable assumption because the softening reactions are fast and atmospheric  $\text{CO}_2$  exchange is relatively slow.

Another assumption is that an equilibrium condition between the solid and dissolved species is reached, regardless of the degree of supersaturation, the presence of seed crystals, or time. This may or may not be true, depending on the kinetics of precipitation. The last major assumption is that the system is electrically neutral, i.e. the sum of all charged species is equal to zero. The units of all species hereafter are mol/L, except for  $C_A$  and  $C_B$ , which are in equivalents/L.

To begin modeling, the initial conditions of the major species of interest must be established. The initial calcium ( $[Ca^{+2}]_0$ ) and total hardness ( $TH_0$ ) values are necessary and are easily measured by compleximetric titration methods (see Chapter 3). From these measurements, the initial magnesium hardness ( $[Mg^{+2}]_0$ ) can be calculated as follows:

$$[Mg^{+2}]_0 = TH_0 - [Ca^{+2}]_0 \quad (2-13)$$

The initial pH and alkalinity ( $Alk_0$ ) are also required. From these measurements, the total carbonic acid species concentration ( $C_{T0}$ ) can be calculated by

$$C_{T0} = \frac{Alk_0 - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2} \quad (2-14)$$

where the ionization fractions ( $\alpha_1, \alpha_2$ ) are calculated using Equations 2-10 and 2-11, respectively, and the hydroxide ion concentration is determined using the ion product of water ( $K_w$ ) as follows:

$$[OH^-] = \frac{K_w}{[H^+]} \quad K_w = 1.00 \times 10^{-14} @ 25^\circ C \quad (2-15)$$

The quantity ( $C_B - C_A$ ) is used to account for any species not explicitly listed but maintains electrical neutrality. This term can be calculated using

$$(C_B - C_A)_0 = Alk_0 - 2TH_0 \quad (2-16)$$

When the initial water conditions are known, the next step in the model is to account for the addition of whichever base is chosen to soften the water. If lime (CaO) is chosen, the calcium concentration must be adjusted to account for the addition of CaO as

$$[Ca^{+2}]_o^* = [Ca^{+2}]_o + [CaO]_{added} \quad (2-17)$$

For the addition of caustic soda (NaOH), the following adjustment must be made for the additional sodium in solution:

$$(C_B - C_A)_o^* = (C_B - C_A)_o + [NaOH]_{added} \quad (2-18)$$

For the addition of soda ash (Na<sub>2</sub>CO<sub>3</sub>), the following adjustment must be made for the additional sodium in solution:

$$(C_B - C_A)_o^* = (C_B - C_A)_o + 2[Na_2CO_3]_{added} \quad (2-19)$$

In addition, when adding soda ash, the carbonate concentration must be adjusted as follows:

$$C_{To}^* = C_{To} + [Na_2CO_3]_{added} \quad (2-20)$$

Once the initial species are accounted for, the equilibrium conditions can be determined for the addition of any softening agents using an overall charge balance and solubility considerations. The charge balance for the major constituents in accordance with Eqn. 2-12 becomes

$$2[Ca^{+2}] + 2[Mg^{+2}] + [H^+] + (C_B - C_A) = C_T(\alpha_1 + 2\alpha_2) + [OH^-] \quad (2-21)$$

The solubility expressions for calcium carbonate and magnesium hydroxide, given by Eqns 2-3 and 2-4, provide the closure relationships.

The purpose of this model is to determine the residual [Ca<sup>+2</sup>], [Mg<sup>+2</sup>], and final pH for incremental additions of base, which is accomplished by calculating the amount of calcium carbonate precipitated, the amount of magnesium hydroxide precipitated, and the

subsequent equilibrium pH. The three equations necessary to solve for these unknowns are the charge balance and the two solubility expressions.

For the case of calcium carbonate, the amount of precipitate ( $P_{CaCO_3}$ ) for any incremental addition of base can be determined starting with

$$[Ca^{+2}] = ([Ca^{+2}]_0^* - P_{CaCO_3}) \quad (2-22)$$

$$[CO_3^{-2}] = [\alpha_2([C_T]_0^* - P_{CaCO_3})] \quad (2-23)$$

$$K_{so, CaCO_3} = ([Ca^{+2}]_0^* - P_{CaCO_3})[\alpha_2([C_T]_0^* - P_{CaCO_3})] \quad (2-24)$$

$P_{CaCO_3}$  can be found by solving the solubility expression as a quadratic equation

$$(P_{CaCO_3})^2 + P_{CaCO_3}(-[Ca^{+2}]_0^* - [C_T]_0^*) + \left[ [Ca^{+2}]_0^* [C_T]_0^* - \frac{K_{so, CaCO_3}}{\alpha_2} \right] = 0 \quad (2-25)$$

The positive root of this quadratic can be solved for using the quadratic equation and an initial guess of the pH which translates into a value of  $\alpha_2$ .

In a similar manner, the magnesium hydroxide precipitated ( $P_{Mg(OH)_2}$ ) for any incremental addition of base can be solved for given an initial guess of the pH as follows:

$$[Mg^{+2}] = ([Mg^{+2}]_0^* - P_{Mg(OH)_2}) \quad (2-26)$$

$$K_{so, Mg(OH)_2} = [Mg^{+2}][OH^-]^2 = ([Mg^{+2}]_0^* - P_{Mg(OH)_2}) \left[ \frac{K_w}{[H^+]} \right]^2 \quad (2-27)$$

$$P_{Mg(OH)_2} = [Mg^{+2}]_0^* - K_{so, Mg(OH)_2} \left[ \frac{K_w}{[H^+]} \right]^{-2} \quad (2-28)$$

The final equation necessary is for  $C_T$ , given as

$$C_T = [C_T]_0^* - P_{CaCO_3} \quad (2-29)$$

Once  $P_{CaCO_3}$  and  $P_{Mg(OH)_2}$  are calculated, the residual  $[Ca^{+2}]$ ,  $[Mg^{+2}]$ , and  $C_T$  can be determined using Eqns. 2-22, 2-26, and 2-29. With values for these species, the

equilibrium pH value can be found by solving the charge balance (Eqn. 2-21) for  $\alpha_2$  by means of a difference minimization scheme ( $LHS - RHS = 0$ ), and then solving Eqn 2-11 for  $[H^+]$  using the quadratic formula. An iterative set of calculations is then performed by solving for the amount of precipitation that occurs along with the resulting pH. For the calculations made in this study, the model and iterative scheme were solved using the Solver function in Microsoft EXCEL.

In summary, for a given set of initial conditions and incremental additions of base, the iterative scheme can be solved in step-wise fashion as follows:

1. Assume a pH
2. Solve for  $P_{CaCO_3}$  and  $P_{Mg(OH)_2}$  (Equations 2-25 and 2-28)
3. Calculate  $[Ca^{+2}]$ ,  $[Mg^{+2}]$  and  $C_T$  (Equations 2-22, 2-26, and 2-29)
4. Solve the charge balance for  $\alpha_2$ , determine pH (Equation 2-21, 2-11)
5. Repeat until the change from first pH (1) to final pH (4) is negligible

An example of the precipitative softening model is presented in Appendix 1.

## 2.3 Crystallization of Calcium Carbonate

### 2.3.1 Saturation

In order for a solid to precipitate from solution, the solution must be oversaturated with respect to its dissolved constituents. The solubility constant of calcite, defined in Eqn. 2-3, is used to determine the level of saturation ( $\Omega$ ) based on the free energy of dissolution, as given by

$$\Delta G = RT \ln \left( \frac{(a_{\text{Ca}^{+2}})_{\text{act}} (a_{\text{CO}_3^{-2}})_{\text{act}}}{(a_{\text{Ca}^{+2}})_{\text{eq}} (a_{\text{CO}_3^{-2}})_{\text{eq}}} \right) = RT \ln \left( \frac{\text{IAP}}{K_{\text{so}}} \right) = RT \ln \Omega \quad (2-30)$$

where  $R$  is the ideal gas constant,  $T$  is absolute temperature,  $(a_{\text{Ca}^{+2}})_{\text{act}}$  and  $(a_{\text{CO}_3^{-2}})_{\text{act}}$  are the actual activities of calcium and carbonate ions in solution, respectively,  $(a_{\text{Ca}^{+2}})_{\text{eq}}$  and  $(a_{\text{CO}_3^{-2}})_{\text{eq}}$  are the equilibrium activities of calcium and carbonate ions, respectively, and IAP is the ion activity product. Assuming that the activities of these species are approximately equal to their molar concentrations allows Eqn. 2-30 to be written as

$$\Delta G = RT \ln \left( \frac{[\text{Ca}^{+2}]_{\text{act}} [\text{CO}_3^{-2}]_{\text{act}}}{[\text{Ca}^{+2}]_{\text{eq}} [\text{CO}_3^{-2}]_{\text{eq}}} \right) = RT \ln \left( \frac{\text{IAP}}{K_{\text{so}}} \right) = RT \ln \Omega \quad (2-31)$$

By comparing the actual ion activity product (IAP) to the solubility product ( $K_{\text{so}}$ ), the degree of saturation ( $\Omega$ ) is defined as follows: for  $\Omega > 0$ , the solution is oversaturated ( $\text{IAP} > K_{\text{so}}$ ), and precipitation is thermodynamically favored ( $\Delta G > 0$ )\*. For  $\Omega < 0$ , the solution is undersaturated ( $\text{IAP} < K_{\text{so}}$ ) and dissolution of solid is thermodynamically favored ( $\Delta G < 0$ ). If  $\text{IAP} = K_{\text{so}}$ , then the system is at equilibrium and  $\Delta G = 0$ .

\*  $\Delta G$  is positive since the reaction in 2-31 is written as a dissolution reaction.



While precipitation will only occur for oversaturated solutions, supersaturation *does not* guarantee spontaneous precipitation. An oversaturated situation only means that precipitation is thermodynamically favored, not that it is imminent. The kinetics of precipitation are discussed in the following section.

### 2.3.2 Nucleation

The crystallization of calcium carbonate involves the transition of dissolved calcium and carbonate in oversaturated solutions into a solid phase through a process called nucleation. Nucleation corresponds to the formation of new centers from which spontaneous crystal growth can occur [8]. Nucleation can be homogenous or heterogeneous, depending on the absence or presence of any solid substrates that can act as seeds to provide surfaces for crystal growth.

Homogenous nucleation involves the precipitation of solids in the absence of a foreign surface. As dissolved species in oversaturated solutions encounter each other, they form clusters. The surface energy associated with the formation of these clusters provides the resistance to crystal growth. Once a cluster of critical size is formed, this energy barrier is overcome and nucleation can occur. Because of the inherent dependence on the frequency of ion cluster encounters, homogenous nucleation does not extensively occur even over very long time spans for a supersaturation ( $\Omega \leq 10$ ) [8]. However, this does not mean that the rate of precipitation for a solution with a supersaturation  $\Omega \geq 10$  will be fast. The precipitation rate of calcium carbonate is directly proportional to the product of calcium and carbonate ion concentration (IAP).

This rate is independent of stirring speed, eliminating diffusion control as a possible rate limiting step [9].

Heterogeneous nucleation occurs in the presence of any solid substrate that provides a surface for crystal growth. The presence of a solid substrate can serve to catalyze the crystallization process by lowering the free energy associated with nucleation. This is especially true of the formation of a surface nucleus on a seed crystal of the same mineral because the interfacial energy between the cluster and seed crystal is smaller than the interfacial energy between the cluster and solution. Different seed crystals will lower the free energy of nucleation by differing degrees depending on the surface characteristics of the seed crystal. The ideal case is when a seed crystal consists of the dissolved species to be precipitated.

Often there is a time lag before nucleation occurs. This is due to the interfacial energy barrier between the ion cluster and the solvent that must be overcome. The time required for nucleation is the time necessary for the ion clusters to reach their critical size and form nuclei, after which crystal growth proceeds rapidly. For carbonates, the energy barrier decreases with increasing degree of supersaturation. This means that nucleation will occur faster as the degree of supersaturation increases.

It is generally agreed that calcite grows by a surface reaction mechanism [10] and that these reactions are kinetically controlled processes in natural waters [11]. Once nuclei form in a supersaturated solution, the concentration of the dissolved material decreases as both nucleation and crystal growth occur. The more rapid the nucleation process, the larger the number of nuclei formed before relief of the supersaturation occurs and the smaller the final crystal size [12].

### 2.3.3 Crystal Growth Retardation/Inhibition

Nucleation and crystal growth occur at the interfaces between clusters and solid surfaces, and so dissolved foreign constituents that can prevent such encounters may interfere with these processes. Because of the site-specific nature of crystal growth interference, molecular size, and stereochemistry of these foreign constituents are important factors [6]. Trace concentrations of dissolved organic matter and orthophosphate can act as "crystal poisons" in the nucleation and growth of calcite, probably by becoming adsorbed on active growth sites [8]. It has also been noted that some crystal poisons can retard crystal dissolution in undersaturated systems.

Calcium carbonate crystal growth inhibition has been demonstrated in the presence of common ions such as  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+3}$ , and  $\text{PO}_4^{-3}$  [10]. The pH at which the zeta potential or surface charge of calcite is zero ( $\text{pH}_{\text{ZPC}}$ ) is 8.2 [13]. Because the zeta potential of calcite is negative for the pH values encountered in softening [14], it could be expected that positive ion adsorption (e.g.  $\text{Mg}^{+2}$  and  $\text{Fe}^{+3}$ ) would have a greater effect on calcite crystal growth inhibition. In addition to charge considerations, dissolved species that undergo specific chemical adsorption at the calcite surface will inhibit crystal growth (e.g.  $\text{PO}_4^{-4}$  and dissolved organic matter) by forming chemical bonds at the calcite surface, thereby retarding crystal growth.

Inorganic constituents can also influence calcite crystal growth through coprecipitation. Coprecipitation involves the precipitation of two species with one of them eventually occluded within the other. Coprecipitation of trace elements such as magnesium, manganese, and strontium within the calcite crystal lattice can influence the

growth mechanism, rate, and final crystal structure of calcium carbonate [15]. Research has shown that the calcite growth rate is reduced by the presence of  $Mg^{+2}$ , and the higher the Mg/Ca ratio in the solution, the lower the growth rate of calcite in a supersaturated solution [16].

#### **2.3.4 Natural Organic Matter Interactions**

Natural organic matter (NOM) is a ubiquitous constituent of surface and ground waters. Because NOM is derived from the decay of terrestrial and aquatic vegetation, it is highly variable in nature and depends on the characteristics of the vegetation and vegetative decay processes in the watershed. In addition, the characteristics of aquatic NOM taken from different locations or during different seasons will most likely vary with respect to molecular weight, functional group content, and acidity. The complex structure(s) of NOM give it a multifunctional role in aquatic systems, including serving as an electron donor in metal complexation and adsorption reactions onto mineral faces [17].

Because of its adsorptive tendency, dissolved organic material (DOM) has been shown to be an effective crystal growth inhibitor [10]. The degree to which DOM can adsorb to calcite surfaces and thereby inhibit crystal growth is dependent on its functional group characteristics and the pH. Aromatic moieties exhibit the highest degree of inhibition, followed by carboxylic groups, and finally aliphatic moieties [10]. In addition, larger molecules of DOM may adsorb to more than one growth site on a mineral surface. In terms of dissolved organic carbon (DOC), a surrogate for DOM, calcite precipitation has been shown to be completely inhibited in the supersaturation range of 1-24 when the DOC concentration was 0.3 mM or greater [11].

In addition to surface adsorption, the phenolic and carboxylic acid functional groups of dissolved organic matter have the capacity to complex  $\text{Ca}^{+2}$  in the solution phase, depending on the pH and nature of the DOM. If  $\text{Ca}^{+2}$  is bound to DOM, this reduces the degree of supersaturation for calcium carbonate. However, this effect has been considered to be insignificant in previous research due to the small degree of  $\text{Ca}^{+2}$  binding by DOM in natural waters [10]. Carboxylic groups are thought to have  $K_a$  values on  $10^{-3}$  to  $10^{-6}$ , while the phenolic groups have a  $K_a$  on the order of  $10^{-9}$  to  $10^{-13}$  [8].

## 2.4 Water Softening in Practice

The basic goal of water softening by chemical precipitation is to raise the solution pH so that bicarbonate ions are converted to the carbonate form and the solubility product of  $\text{CaCO}_{3(s)}$  is exceeded. This is usually achieved through the addition of lime because of its availability and cost. If the original carbonate concentration is not high enough to effectively precipitate all of the calcium in solution, soda ash ( $\text{Na}_2\text{CO}_3$ ) is added. The four process types and the conditions that dictate their choice are given as [1]:

1. Single-stage lime process: Source water has high calcium, low magnesium carbonate hardness (less than 40 mg/L as  $\text{CaCO}_3$ ), and no noncarbonate hardness.
2. Excess lime process: Source water has high calcium, high magnesium carbonate hardness, and no noncarbonate hardness. Excess lime is added to raise the pH above 11 to remove the magnesium hardness.
3. Single-stage lime-soda ash process: Source water has high calcium, low magnesium carbonate hardness (less than 40 mg/L as  $\text{CaCO}_3$ ). Some calcium non-carbonate hardness.

4. Excess lime-soda ash process: Source water has high calcium, high magnesium carbonate hardness and some noncarbonate hardness. It may be a one- or two-stage process.

Water that has undergone treatment through one of these processes must be recarbonated. The process of recarbonation lowers the pH and stabilizes the water to prevent deposition of hard carbonate scale on filter sand and distribution piping. Recarbonation is achieved by adding carbon dioxide gas to the treated water until the pH is in the range of 8.4 to 8.6 [1].

Typically treatment plants that employ chemical precipitation involve the addition of lime or lime and soda-ash in a rapid-mix stage, followed by a slow-mix stage where precipitation and crystal growth can occur, and a sedimentation stage for particle removal. Iron and aluminum salts have been added during lime softening as a settling aid and to increase color removal. If coagulants such as alum, ferric sulfate, or polymers are to be added to enhance the effectiveness of the softening process, these flocculation aids are added after lime addition in the rapid-mix stage to allow the lime time to dissolve.

Current design favors the use of three or more compartments for the slow-mix stage, with decreasing mixing velocity in each subsequent chamber [1]. A minimum retention time of 30 minutes is recommended for conventional water softening. Sludge return to the head of the slow mix stage will reduce chemical requirements as well as provide nuclei for precipitative growth. The estimated portion of returned sludge is 10 to 25 percent of the source water flow [1].

To ensure efficient removal of precipitates formed in the softening process, retention times in the sedimentation stage usually range from 1.5 to 3 hours [1]. Sludge



blanket clarifiers which combine mixing and sludge recirculation are often used in water softening. The recirculated settled sludge provides additional particles that increase the probability of particle contact and nuclei for growth [1]. The sludge produced during water softening is predominantly calcium carbonate or a mixture of calcium carbonate and magnesium hydroxide, which are generally dense, stable, and inert materials that dry well [1].

Fluidized bed reactors such as pellet reactors are also employed to soften water. These systems involve conical reactors in which the presence of a suspended bed of fine sand 0.1 mm to 0.2 mm in diameter acts as a catalyst [1]. Source water and chemicals enter tangentially at the bottom of the cone and rise through the reactor in a swirling motion with an upward velocity that is sufficient to keep the sand fluidized. Precipitated hardness particles attach to the surface of the sand grains so that the grains increase in diameter and eventually pass out of the bottom of the reactor.

Another softening process named compact accelerated precipitation softening (CAPS) involves accelerated  $\text{CaCO}_3$  nucleation and growth [18]. Hard water first passes through a slurry made of small calcite particles where the majority of precipitation takes place. Secondly, the water passes through a  $\text{CaCO}_3$  cake formed on the top of a filter. The cake process serves as a polishing step in which the calcium concentration is further reduced. CAPS may be used as a stand-alone water treatment process or in conjunction with pressure and electrical driven membrane processes as an effective pretreatment routine.

## **CHAPTER 3: METHODS AND MATERIALS**

Several waters, both simulated hard water and real water, were softened in batch experiments using lime (CaO) and caustic soda (NaOH). Caustic soda was used to illuminate the effects of seed crystals primarily because it was completely dissolved; the lime was added as a slurry, somewhat negating the impact that seed crystals produce. Parallel experiments were conducted with seed crystals, including reagent-grade Fisher calcium carbonate, Procter and Gamble proprietary calcium carbonate, and for real waters, the dried softening sludge from that source water's respective treatment plant. The dissolved calcium, total calcium, total hardness, and pH were measured to determine softening effectiveness.

### **3.1 Materials**

#### **3.1.1 Raw Water**

Experiments were conducted with a model water of moderate hardness and two real waters from across the United States. The real waters were selected so that different initial hardness and TOC levels were represented; Table 3.1 lists the parameters of interest from each of the waters used in this study. Waters were shipped from the respective utilities in 40-gallon drums and refrigerated at 40 °F immediately upon their arrival. Before testing, an appropriate amount of water in a sealed flask was allowed to come to room temperature (22 °C) over a 24-hour period.



Table 3.1  
Raw Water Characteristics

Source	Total Hardness (mg/L as CaCO <sub>3</sub> )	Calcium Hardness (mg/L as CaCO <sub>3</sub> )	Total Alkalinity (mg/L as CaCO <sub>3</sub> )	TOC (mg/L as C)	pH
Simulated Hard Water	185 - 195	185-195	185-195	0 or 5	7.9-8.2
Parsons Avenue Water Plant Columbus, Ohio	465	324	270	1.4	7.3
Hialeah Water Treatment Facility Miami, Florida	232	207	227	13	7.3

The simulated hard water was made with reagent-grade CaCl<sub>2</sub> and NaHCO<sub>3</sub> (Fisher Chemical Co., Fairlawn, NJ) in organic-free deionized water (OFDW; Dracor, Durham, NC). Stoichiometric amounts of CaCl<sub>2</sub> and sodium bicarbonate were added to the water to achieve a calcium concentration of 200 mg/L as calcium carbonate and a total carbonate concentration of 200 mg/L as calcium carbonate. The actual measured initial concentration of calcium ranged from 185 to 195 mg/L as calcium carbonate and the actual measured initial concentration of bicarbonate ranged from 185 to 195 mg/L as calcium carbonate. The initial pH of the model water ranged from 7.9 to 8.2. The model water was prepared 24 hours before testing and allowed to come to room temperature in a sealed flask. All solids were weighed on a digital Sartorius Balance (Basic Model).

In some cases, natural organic matter was added to the model waters at a concentration of 5 mg/L as C. The NOM consisted of fulvic acid, originally isolated from Lake Drummond, Virginia in August, 1985 (Reckow Thesis, UNC); it had been stored in dry form as a powder in a sealed vial.

### 3.1.2 Seed Characteristics

In order to study the effects of seed crystals, different seeding agents were explored, including reagent grade calcium carbonate (Fisher Chemical Co., Fairlawn, NJ), the Procter and Gamble proprietary calcite seed (see Chapter 1), and for the utility-provided waters, the dried sludge collected from their treatment plants. The Procter and Gamble seed crystals were crushed before use to expose fresh surfaces.

The utilities shipped the sludge in plastic containers of various sizes. They were refrigerated at 40 °F immediately upon their arrival. Seed crystals of dried sludge were prepared by first allowing a 500 mL sample of the sludge to settle (thicken) for 24 hours. After settling, the supernatant water was decanted carefully so as not to disturb the solids. The solid portion was then dried in an oven at 35°C for 24 hours.

Surface area analysis was done by Micrometrics, Inc (Norcross, GA). The sample was first degassed to remove any adsorbed contaminants that would have made the surface and pores inaccessible to measurement. The surface area analysis was conducted using an adsorption isotherm. Nitrogen was used as the adsorptive gas, and was delivered to the sample at different pressures in order to determine the rate at which it was adsorbed. The sample was allowed to equilibrate at each pressure before the pressure was changed. In this way, an isotherm plot of the relative pressure ( $P_{N_2}/P_0$ ) vs. volume adsorbed ( $\text{cm}^3/\text{g}$ ) was created. The specific surface area characteristics of the seed crystals used in this study are summarized Table 3.2.

Table 3.2

## Specific Surface Area of Seed Crystals

Seed Crystal	BET Surface Area (m <sup>2</sup> /g)
Reagent-Grade Fisher Seed	0.278
Procter and Gamble Seed	2.572
Columbus, OH Sludge Solids	4.316
Hialeah, FL Sludge Solids	1.679

### 3.2 Softening Experiments

Softening experiments were conducted using a Phipps and Bird six-place gang stirrer (Phipps and Bird, Richmond, VA) using stainless steel blades (2.5 cm x 5 cm). The jars were 600-mL glass beakers equipped with sampling ports approximately five centimeters from the bottom of each beaker. The gang stirrers and beakers were placed on an illuminated platform for better observation of the experiment as it was in progress.

Because the purpose of this investigation was to examine the effects of seeding agents, all experimental equipment had to be perfectly clean and free of any foreign surfaces that might act as seed crystals. The jars were cleaned after every use by rinsing with tap water, brushing while rinsing with tap water, rinsing with dilute sulfuric-acid (1.6 M), rinsing with tap water, scrubbing with ALCONOX Detergent, rinsing with tap water, and finally rinsing with OFDW. The jars were then placed upside-down to allow them to dry. All other glassware was washed in a similar manner, as were the stainless steel stirrers.

Stock solutions of lime at a concentration of 4.6 g/L were made from CaO (Fisher Chemical Co., Fairlawn, NJ) the day of use. The lime slurry was continuously mixed in a closed vessel for one hour prior to dosing. It was also well mixed during testing so that the lime added to the jars was uniformly suspended. Stock solutions of NaOH at a concentration of 2.5 g/L were made from NaOH (Fisher Chemical Co., Fairlawn, NJ) previous to experimentation and stored for no longer than two weeks in sealed vessels; mixing of these solutions was deemed unnecessary as the constituents were completely dissolved. The concentration of the doses of these stock solutions varied according to the water being tested.

The pH, calcium hardness, alkalinity, and total hardness (if applicable) of the raw water were initially determined; these values were used to model the softening process and determine the base doses used during testing. Up to six jars, each with 500 mL of water, were then placed beneath the gang stirrers. Stirring commenced at 100 rpm. If a crystal seed was being tested, it was added rapidly to each jar and then followed by the addition of base. The jars were mixed at 100 rpm for three minutes following the first addition of base. After the rapid mix, the jars were mixed slowly at 55 rpm for thirty minutes and then allowed to settle quiescently for 10 minutes. This settling time was chosen to simulate an overflow rate of  $13 \text{ m}^3/\text{m}^2\text{-d}$  (typical lime softening overflow rates are about  $50 \text{ m}^3/\text{m}^2\text{-d}$  [7]).

After settling, approximately 50 mL of the supernatant was wasted to wash out any solids that might have accumulated in the sampling port. A 250 mL sample of the supernatant was drawn out and later split for analysis of calcium (dissolved and total), total hardness, and pH as described in the analysis section that follows.

### **3.3 Analysis**

#### **3.3.1 pH**

An Accumet 10 pH Meter (Fisher Scientific, Pittsburgh, PA) was used to measure pH. The meter was calibrated frequently using pH 4,7, and 10 buffer solutions (Fisher Chemical Co., Fairlawn, NJ), and was calibrated daily at a pH of 7. Prior to each use, the probe was rinsed with OFDW and dried with a Kimwipe.

#### **3.3.2 Alkalinity**

The Standard Titration Method for Alkalinity [6] was employed to determine alkalinity based on carbonate and bicarbonate content. Samples were titrated to the appropriate end-point pH with a standard solution of 0.02 N  $\text{H}_2\text{SO}_4$  (Fisher Chemical Co., Fairlawn, NJ). A bromocresol green-methyl red solution (LabChem Inc, Pittsburgh, PA) was used as an indicator. A 50 mL titration sample was used in all cases.

#### **3.3.3 Dissolved Calcium**

The 250 mL sample of supernatant was shaken and then approximately 75 mL were vacuum filtered through a 0.2  $\mu\text{m}$  NyaFlo nylon membrane filter (Gelman Sciences, Ann Arbor, Michigan). The membrane filter was first wet with OFDW before filtration. Between filtrations, the vacuum flask apparatus was washed and rinsed with OFDW and allowed to dry upside-down. The Standard Titration Method for Calcium [6] using a standard 0.01 M EDTA solution (Fisher Chemical Co., Fairlawn, NJ ) and Murexide Indicator (LabChem Inc, Pittsburgh, PA) was employed to determine the dissolved

calcium concentration. A titration volume of 50 mL was typically used. The solution was first raised to a pH of 12 to 13 by adding a sufficient amount of 1 M NaOH to precipitate any magnesium. The titration was always completed in less than five minutes.

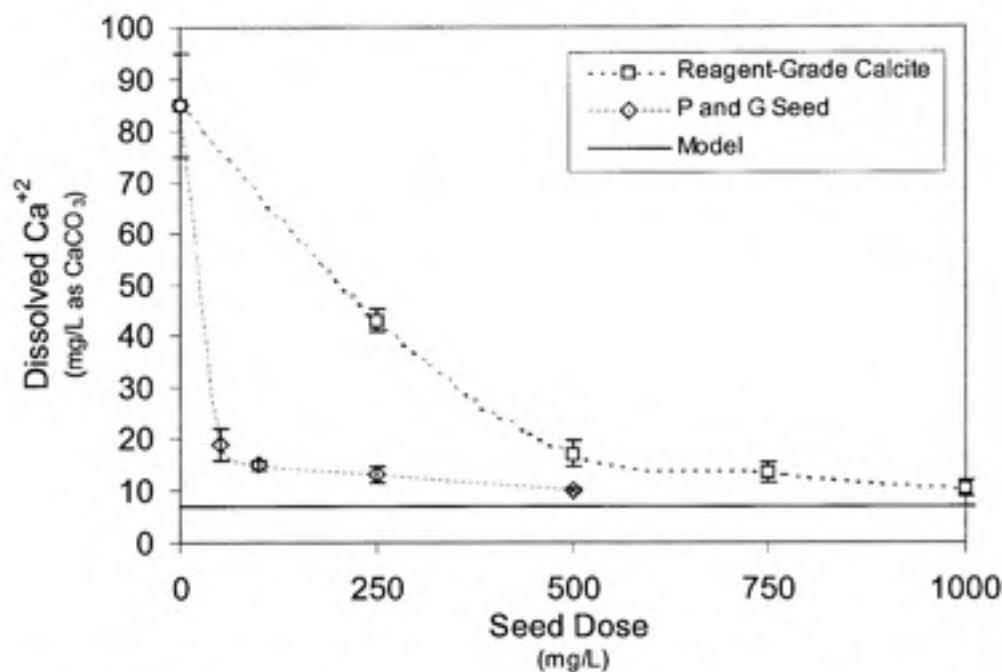
### **3.3.4 Total Calcium (Dissolved + Unsettled $\text{CaCO}_{3(s)}$ )**

150 mL of the shaken supernatant was poured into a 250 mL flask for use in measuring total calcium and total hardness. 20 mL of 0.1 N  $\text{H}_2\text{SO}_4$  (Fisher Chemical Co., Fairlawn, NJ) was added to the water to completely dissolve any  $\text{CaCO}_{3(s)}$  and  $\text{Mg}(\text{OH})_{2(s)}$  suspended in solution. The flasks were then shaken on a L.E.D. Orbit Shaker (Lab-Line Instruments, Inc., Melrose Park, IL) for 24 hours. The Standard Titration Method for Calcium [6] using a standard 0.01 M EDTA solution (Fisher Chemical Co., Fairlawn, NJ ) and Murexide Indicator (LabChem Inc, Pittsburgh, PA) was employed to determine the total calcium (now as dissolved calcium). A titration volume of 50 mL was typically used. The solution was first raised to a pH of 12 to 13 by adding a sufficient amount of 1 M NaOH to precipitate any magnesium. The titration was always completed in less than five minutes.

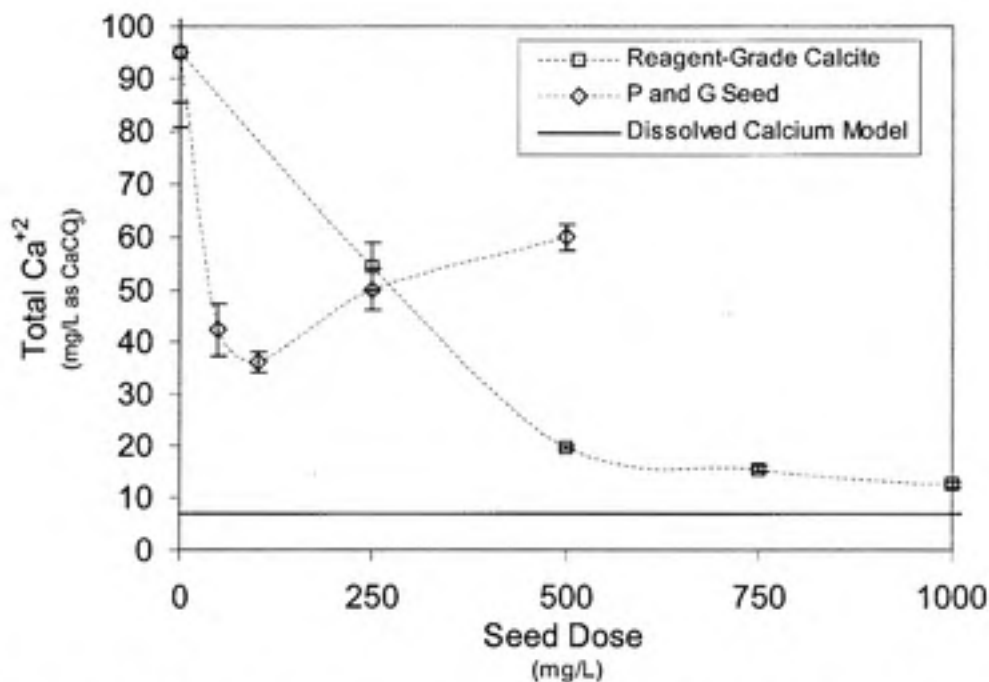
### **3.3.5 Total Hardness**

The Standard Titration Method for Hardness [6] using 0.01 M EDTA (Fisher Chemical Co., Fairlawn, NJ ) and Eriochrome Black T (LabChem Inc, Pittsburgh, PA) was employed to determine total hardness. Approximately 2 mL of buffer solution was added to the titration volume. The buffer was made from 179 g of the disodium salt of EDTA (Fisher Chemical Co., Fairlawn, NJ) and 644 mg magnesium chloride (LabChem

Inc, Pittsburgh, PA) in 50 mL of OFDW added to 16.9 g  $\text{NH}_4\text{Cl}$  (Fisher Chemical Co., Fairlawn, NJ) and 143 mL of concentrated  $\text{NH}_4\text{OH}$  (Fisher Chemical Co., Fairlawn, NJ) diluted to 250 mL. Because the end-point was sharp, no complexing agents were required. Titration volumes of 50 mL or 25 mL were used depending on the amount of hardness. The titration was always completed in less than five minutes.



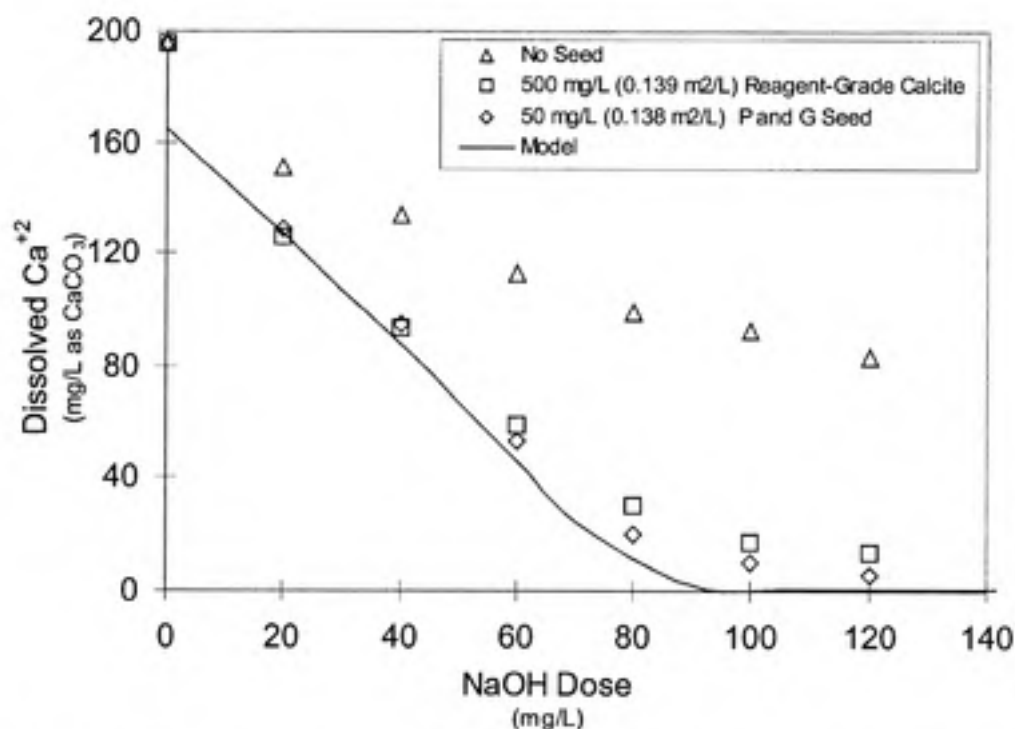
**Figure 4.3** Dissolved calcium concentration resulting from precipitative softening of synthetic water (100 mg/L NaOH) using various doses of reagent-grade calcite and Procter and Gamble seed. The solid line shows the predicted dissolved calcium concentration at equilibrium.



**Figure 4.4** Total calcium concentration resulting from precipitative softening of synthetic water (100 mg/L NaOH) using various doses of reagent-grade calcite and Procter and Gamble seed. The solid line shows the predicted dissolved calcium concentration at equilibrium.



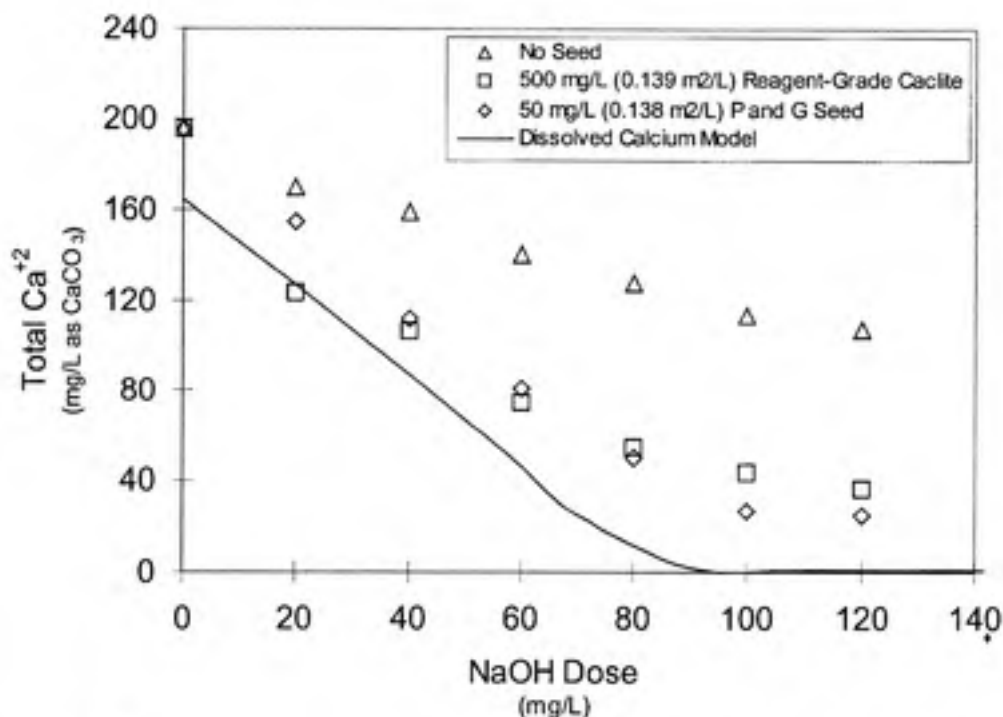
In Figure 4.5, it can be seen that the addition of seed crystals greatly enhances the removal of dissolved calcium, producing dissolved calcium concentrations near those predicted by the equilibrium model. The seed crystals provide the surface area necessary to overcome the barrier against nucleation and growth, and efficient precipitation of dissolved calcium is observed. There is little difference between the results obtained using either seed, which is expected because they have approximately the same surface area and both consist of calcite. Error bars have been omitted but were of the same magnitude as previous figures.



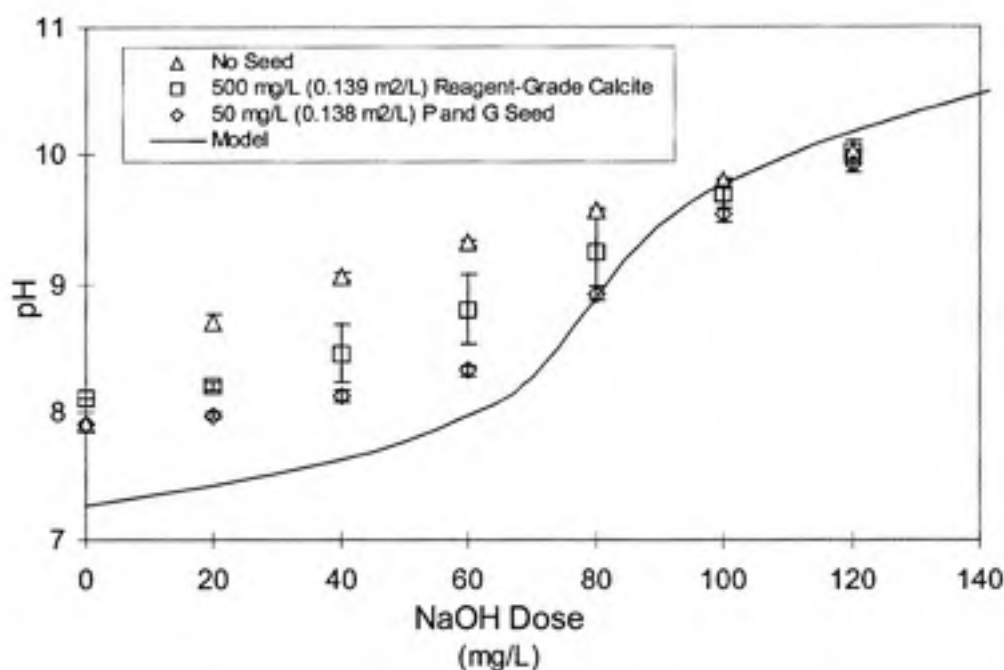
**Figure 4.5** Dissolved calcium resulting from precipitative softening of synthetic water with NaOH, with and without seed crystals. The solid line shows the predicted dissolved calcium concentration at equilibrium.

Figure 4.6 shows that both seed crystals provide much better removal of total calcium than the case where no seed was used. By using these seed crystals at their respective optimal doses, the total calcium concentration approaches the dissolved calcium levels predicted by the equilibrium model. This means that the calcium carbonate that is precipitated settles well in the time allowed. There is little difference with regards to total calcium removal between the reagent-grade calcite and Procter and Gamble seeds at the chosen doses.

Figure 4.7 shows the pH associated with the addition of incremental doses of NaOH. In the absence of any seed crystals, the measured pH differs significantly from that predicted by the equilibrium model. The results obtained when using seed crystals bring the system closer to equilibrium.

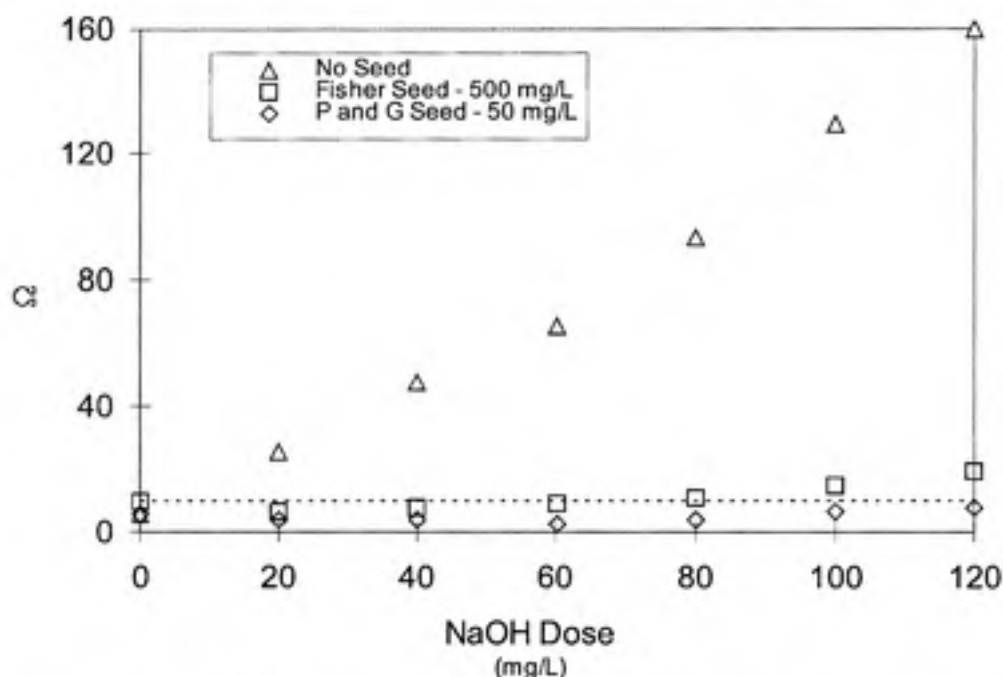


**Figure 4.6** Total calcium resulting from precipitative softening of synthetic water with NaOH, with and without seed crystals. The solid line represents the model predictions for the dissolved calcium.



**Figure 4.7** The pH resulting from precipitative softening of synthetic water with NaOH, with and without seed crystals. The solid line represents the model predictions for the pH.

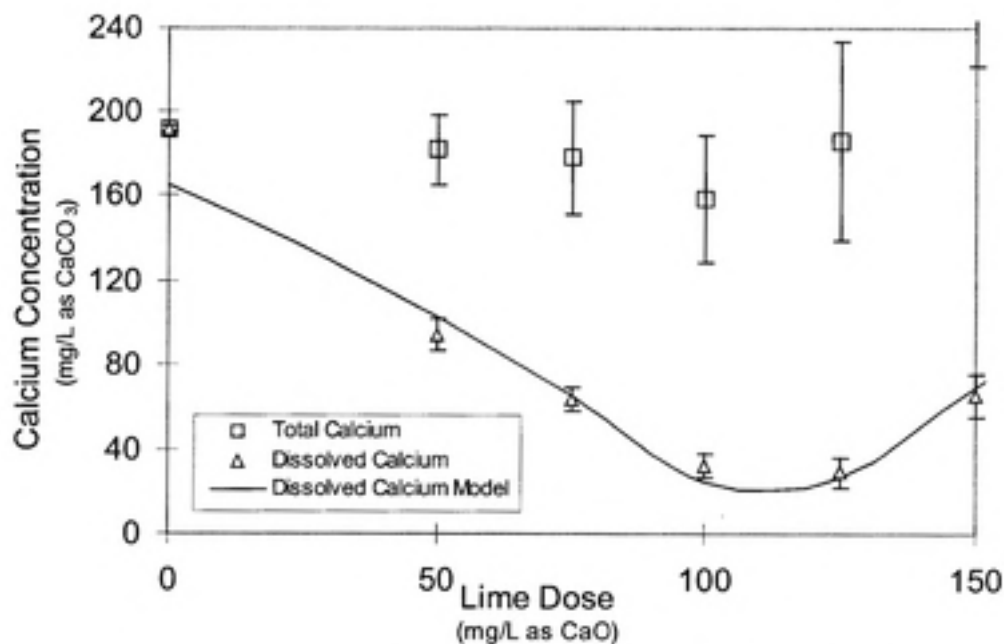
The calcium carbonate supersaturation associated with these experiments is presented in Figure 4.8. The degree of saturation was calculated from the actual data points presented in Figures 4.5 and 4.7 and the  $C_T$  values adjusted for calcite precipitation. For the case with no addition of seed, the supersaturation grows continuously, reaching supersaturation values in excess of 100. For the cases where seed crystals were added, the degree of supersaturation was much lower. Both the reagent-grade calcite and Procter and Gamble seeds produced, for the most part, supersaturation values under 10, with the P and G seed always below this threshold. Equilibrium is not theoretically established until  $\Omega = 1$ . However these calculations assume a temperature of 25 °C, a closed system, and activity coefficients of unity.



**Figure 4.8** The degree of supersaturation resulting from precipitative softening of synthetic water with NaOH, with and without seed crystals. The dashed line shows a degree of supersaturation = 10.

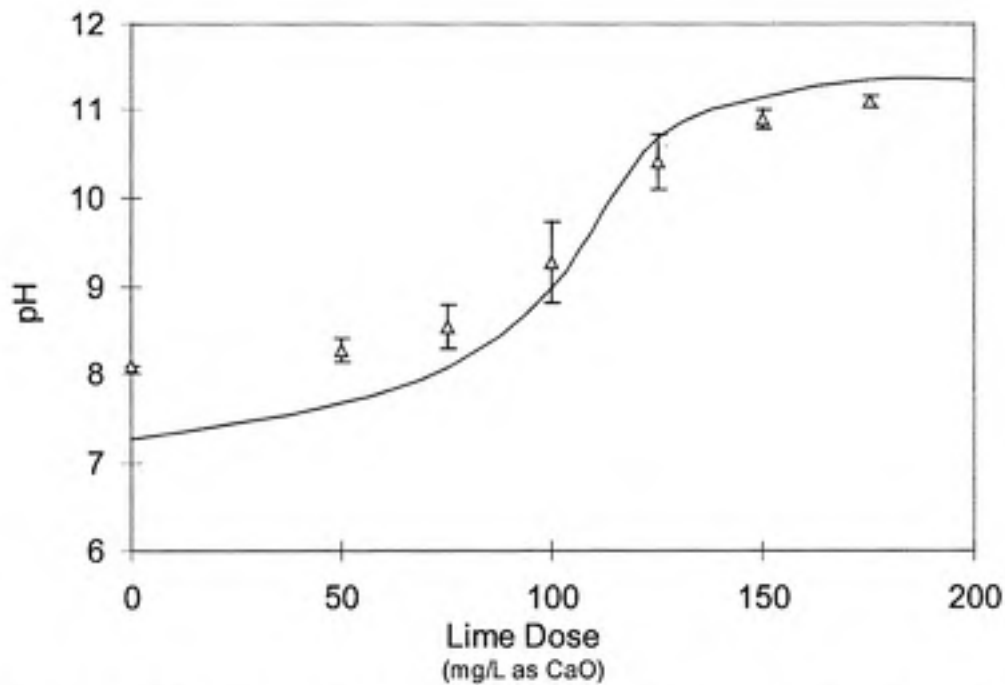
#### 4.1.2 Lime

The model water was softened next with a variety of lime (CaO) doses without the presence of seed crystals. Figure 4.9 shows that measured dissolved calcium concentrations match almost exactly with the dissolved calcium concentrations predicted by the equilibrium model. The reason for this is most likely that the lime particles themselves provide a nucleation surface upon which calcium carbonate can precipitate. The available carbonate for  $\text{CaCO}_3$  precipitation appears to be exhausted for a lime dose of approximately 110 mg/L; subsequent lime addition only serves to raise the dissolved calcium concentration. However, the total calcium concentrations are well above their respective dissolved calcium concentrations, indicating that, although there may be effective precipitation, the settling characteristics of the particles is less than ideal.



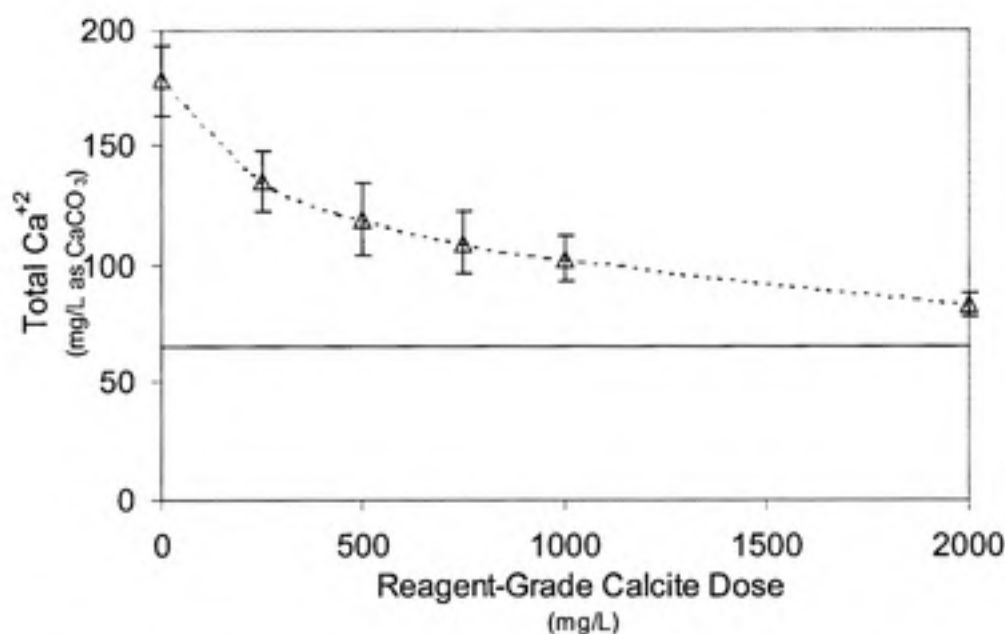
**Figure 4.9** Dissolved and total calcium concentrations resulting from precipitative softening of synthetic water with lime.

Figure 4.10 shows the change in the measured pH and the corresponding model predictions of the equilibrium pH with increasing lime dose. The observed pH matches closely with the model, indicating a close proximity to equilibrium conditions.



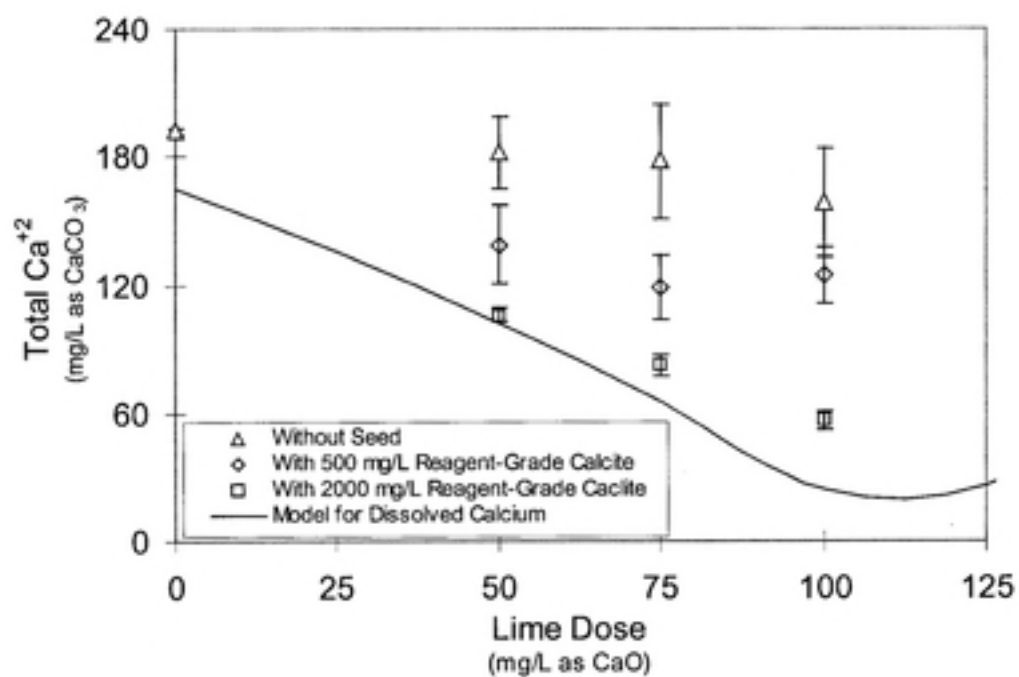
**Figure 4.10** The pH resulting from precipitative softening of synthetic water with lime without seed crystals.

The application of seed crystals was examined to determine if they would lower the total calcium concentration arising from lime softening. It was believed that the seed crystals would increase the size of the precipitate, increasing its ability to settle and thereby lower the total calcium. Figure 4.11 shows the results for the total calcium concentration for a lime dose of 75 mg/L as CaO when the reagent-grade seed dose was varied. Included in this figure is a line representing the model prediction for the dissolved calcium concentration. It can be seen that as the seed dose increases, the total calcium concentration approaches the equilibrium dissolved calcium concentration. This suggests that more of the calcium carbonate precipitate is being removed with increasing seed dose because of increased particle size and better settling.



**Figure 4.11** Total calcium concentration resulting from precipitative softening of synthetic water with various doses of reagent-grade calcite (lime dose of 75 mg/L CaO). The solid line shows the predicted dissolved calcium concentration in accordance with the equilibrium model.

From these results it was determined that the optimal seed dose was on the order of 2000 mg/L. Both this seed dose and 500 mg/L of seed crystals were used to soften the synthetic water with varying doses of lime. The resulting total calcium concentrations are shown in Figures 4.12. As expected, the total calcium concentration is highest when no seed crystals are used and decreases as the seed dose increases. At the highest seed dose, the total calcium concentration approaches the dissolved calcium concentration, indicative of good settling of the precipitated  $\text{CaCO}_3$ .



**Figure 4.12** Total calcium concentration resulting from precipitative softening of synthetic water for various lime and reagent-grade calcite seed doses. The line shows the equilibrium predictions for the dissolved calcium concentration.

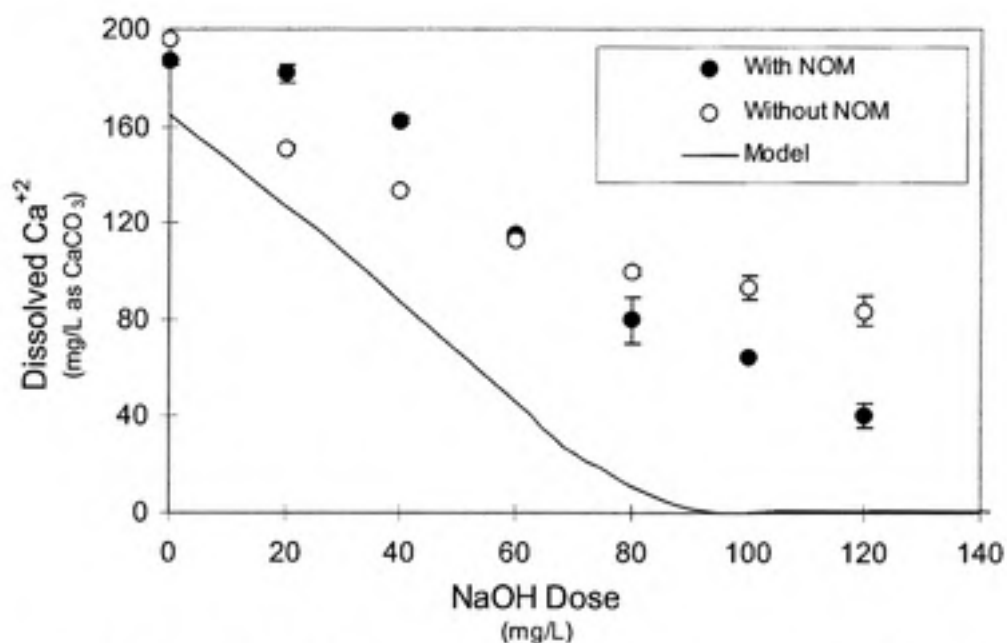


### 4.3 Natural Organic Matter Interactions

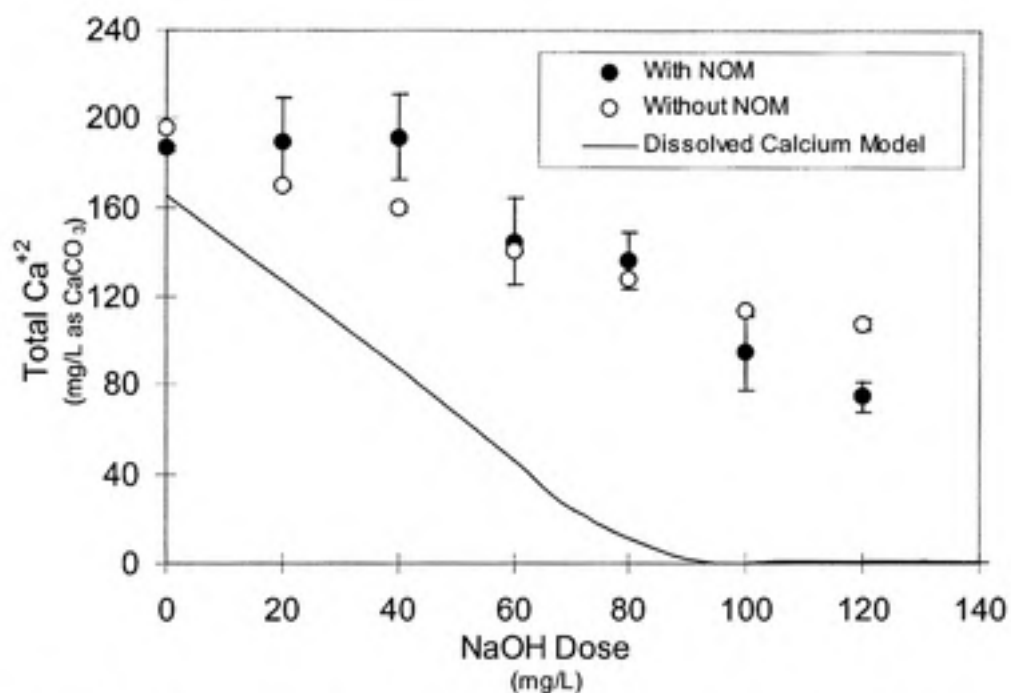
In order to determine the effects of natural organic matter (NOM) during softening, the model water with a calcium hardness and an alkalinity of approximately 200 mg/L as  $\text{CaCO}_3$  and a NOM content of 5 mg/L as C (fulvic acid isolated from Lake Drummond, VA) was softened with NaOH. Tests were conducted both with and without a reagent-grade calcite dose of 500 mg/L ( $0.139 \text{ m}^2/\text{L}$ ).

#### 4.3.1 Comparison of Softening With and Without NOM (no seed crystals)

Figure 4.13 shows that when NOM is present, it appears to inhibit the removal of dissolved calcium at low NaOH doses ( $<60 \text{ mg/L NaOH}$ ,  $\text{pH} < 9.3$ ) while improving dissolved calcium removal at subsequent higher NaOH doses ( $>80 \text{ mg/L NaOH}$ ,  $\text{pH} > 9.7$ ). The inhibition may be the result of the formation of soluble complexes between NOM and calcium, which enhances calcium solubility, or it may be a result of the adsorption of NOM to the surface of the calcium carbonate precipitate, which inhibits nucleation and further crystal growth. The improved precipitation of calcium in the presence of NOM at the higher NaOH doses must be associated with the binding of NOM and  $\text{Ca}^{+2}$  to the growing  $\text{CaCO}_3$  precipitate. Figure 4.14 shows that the total calcium concentration reflects the same changes observed for dissolved calcium; for the lower NaOH doses, the presence of NOM hinders the removal of total calcium, while the opposite is true for higher NaOH doses.

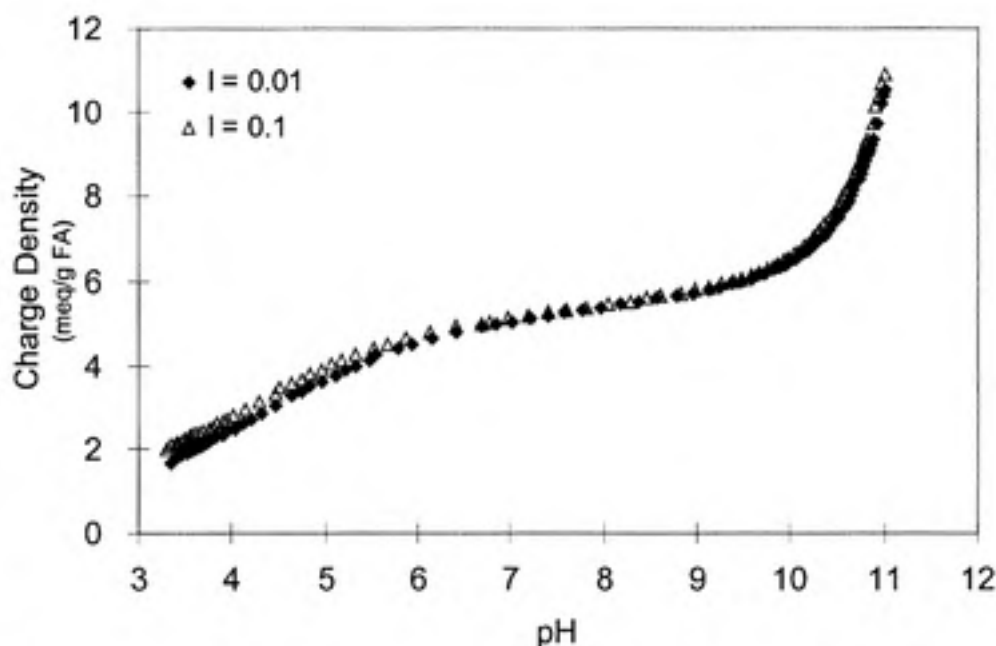


**Figure 4.13** Dissolved calcium concentration resulting from waters softened with caustic soda in the presence and absence of NOM (5 mg/L as C). The solid line indicates the equilibrium model predictions.

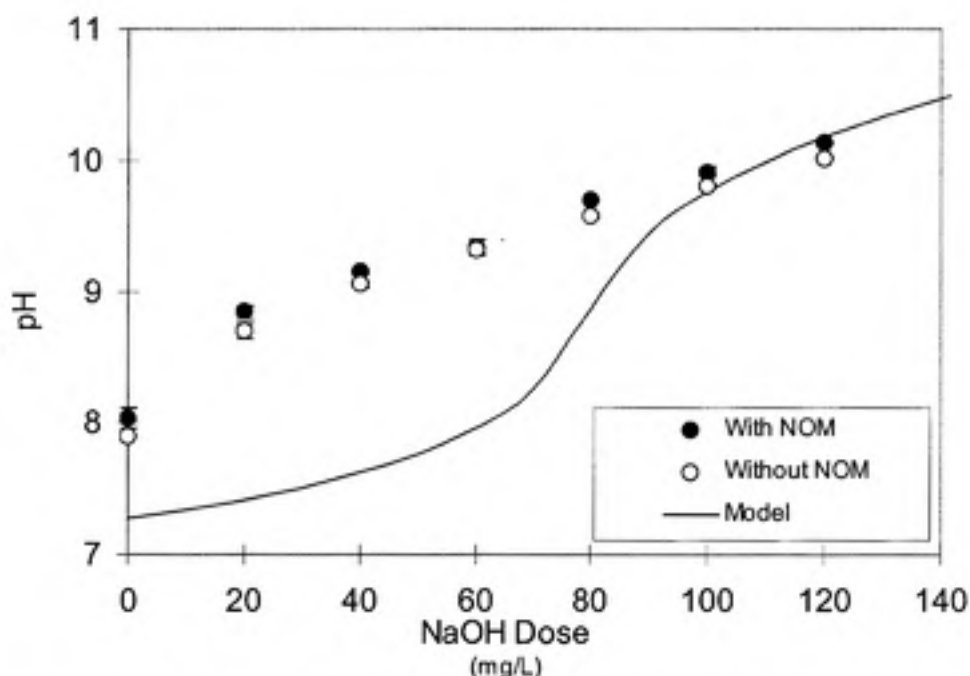


**Figure 4.14** Total calcium concentration resulting from waters softened with caustic soda in the presence and absence of NOM (5 mg/L as C). The solid line indicates the equilibrium model predictions for the dissolved calcium concentration.

Figure 4.15 is an alkalimetric titration curve which shows the charge density of Lake Drummond NOM as a function of pH. This curve was generated by Lin (2002, unpublished) by titrating 150 mg/L of NOM (as C) with NaOH under a  $N_2$  atmosphere. At pH values below pH 7, the increasing charge density is due to deprotonation of carboxylic acid functional groups. Above pH 9.5, the increasing charge density is due to deprotonation of phenolic groups. Because the pH at which NOM appears to aid the precipitation of calcium occurs at  $pH > 9.5$  (see Figure 4.16 for 60 to 80 mg/L of NaOH), the improvement must be associated with the formation of deprotonated phenolic groups.



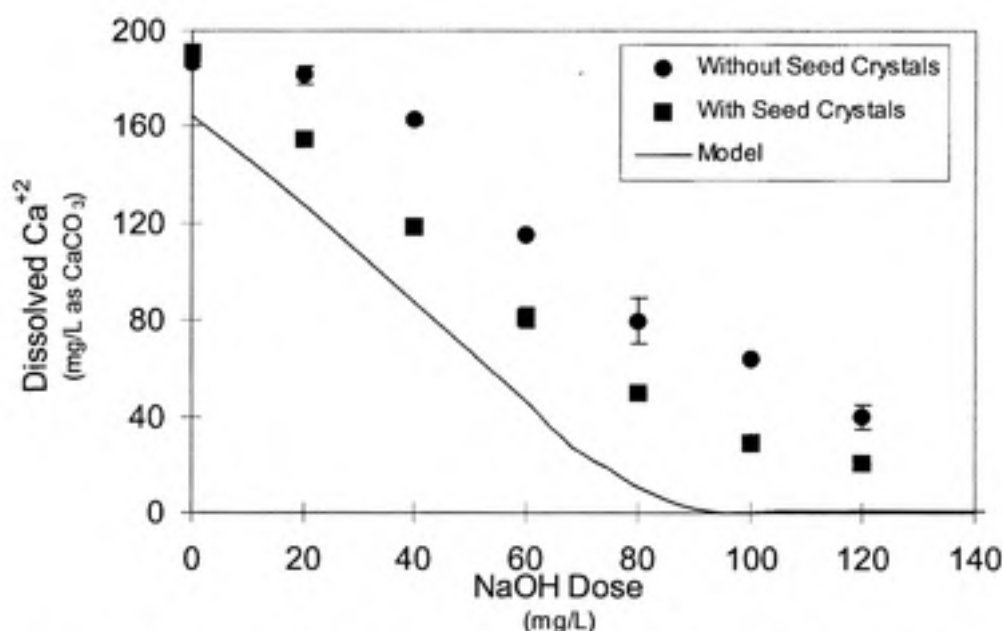
**Figure 4.15** Charge density resulting from titration of 150 mg/L of NOM (as C) (Lake Drummond, VA) with 0.02 N NaOH ( $I$  = ionic strength). Courtesy of Y. P. Lin (2002, unpublished).



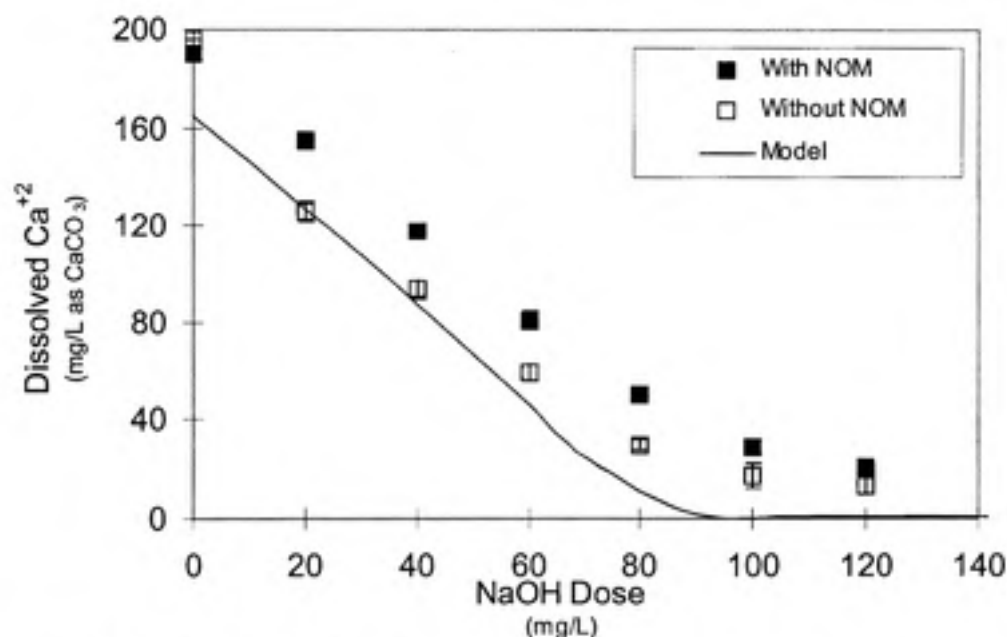
**Figure 4.16** pH resulting from waters softened with caustic soda in the presence and absence of NOM (5 mg/L as C). The solid line indicates the equilibrium model predictions.

#### 4.3.2 Comparison of Softening in the Presence of NOM, With and Without Seed Crystals

Figure 4.17 shows that the presence of seed crystals improves the removal of dissolved calcium over the entire range of caustic soda doses investigated. However, the equilibrium predictions of the model are still not reached, indicating that NOM limits the removal of dissolved calcium. This is illustrated to a further degree in Figure 4.18, where it is seen that the dissolved calcium concentrations in the presence of NOM in seeded solutions departs from the equilibrium levels to a greater degree than in the absence of NOM.



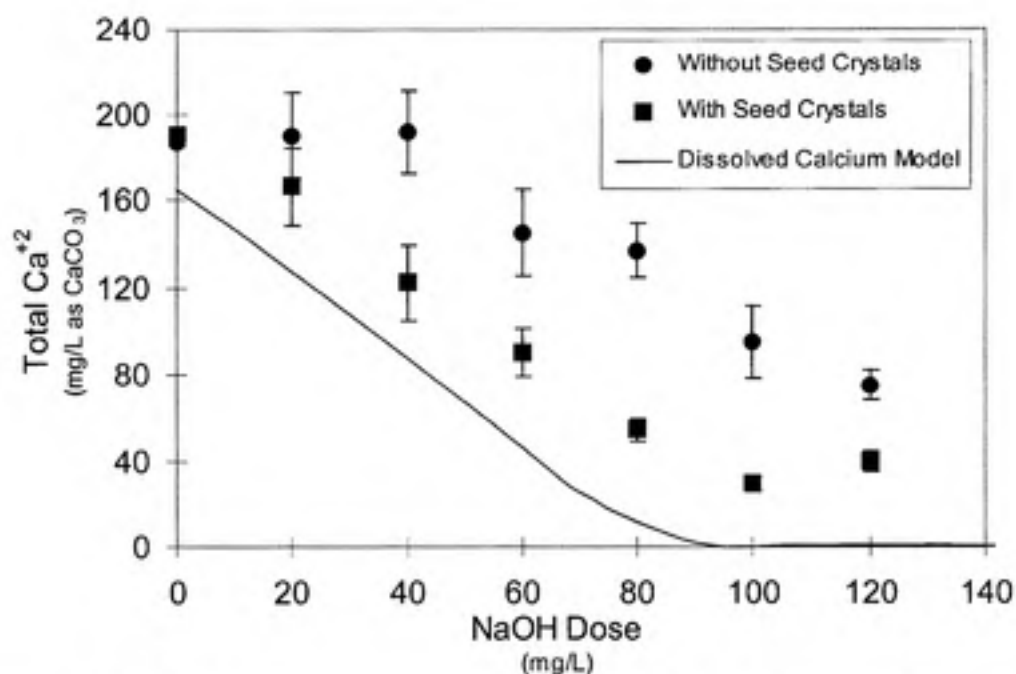
**Figure 4.17** Dissolved calcium concentration resulting from softening with caustic soda in the presence of NOM (5 mg/L as C), with and without seed crystals (500 mg/L reagent-grade calcite). The solid line indicates the equilibrium model predictions.



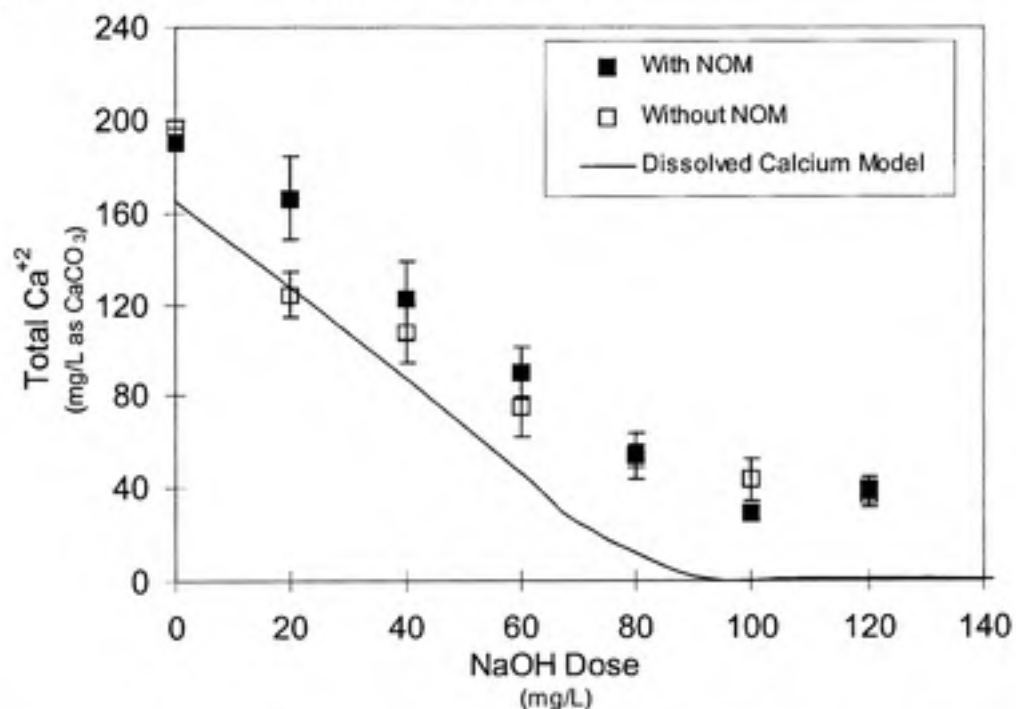
**Figure 4.18** Dissolved calcium concentration resulting from softening with caustic soda with seed crystals (500 mg/L reagent-grade calcite) in the presence and absence of NOM (5 mg/L as C). The solid line indicates the equilibrium model predictions.

Figures 4.19 shows a similar effect for the total calcium concentrations. The results indicate that the presence of seed crystals improves the removal of total calcium, bringing the concentrations closer to those expected using the equilibrium model. However, Figure 4.20 shows that the results with NOM depart from the predicted equilibrium values in the seeded solutions to a further degree than in the absence of NOM, suggesting that the presence of NOM inhibits calcium removal. The calcium carbonate seed provides a much greater surface area than that of the newly precipitated crystals in the absence of any seed.

If NOM is indeed binding to the solid calcium carbonate surface and inhibiting calcium removal, then it would appear that the effects of NOM are minimized in the presence of the seed crystals because there are more nucleation sites available. A greater number of nucleation sites would mean that a lower percent of them are blocked due to the binding with NOM, and therefore more precipitation can occur. Nevertheless, NOM still inhibits the removal of calcium.

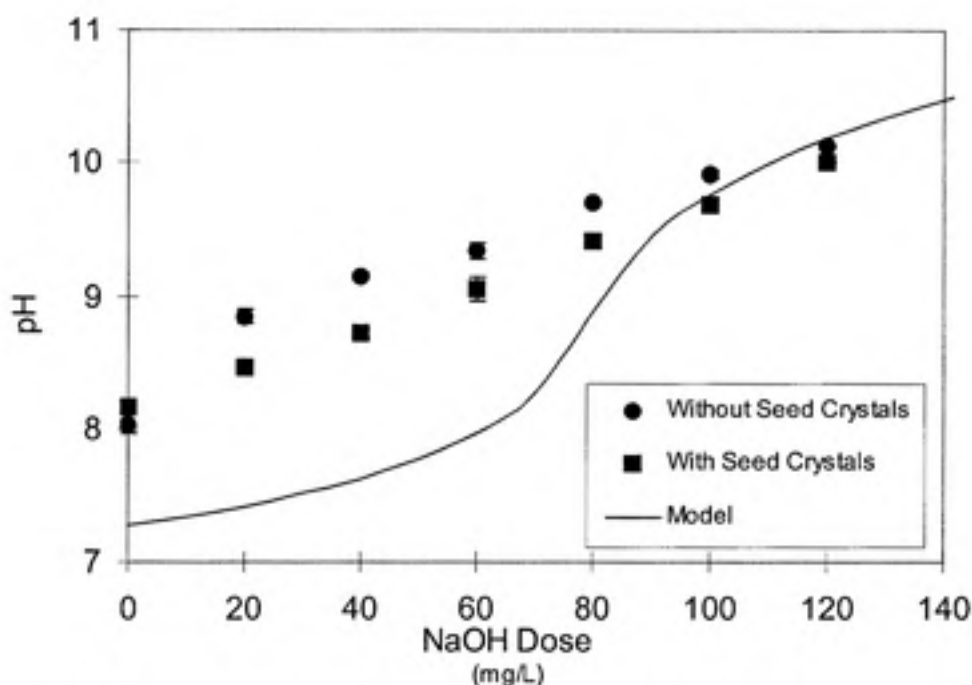


**Figure 4.19** Total calcium concentration resulting from softening with caustic soda in the presence of NOM (5 mg/L as C ), with and without seed crystals (500 mg/L reagent-grade calcite). The solid line indicates the equilibrium model predictions for the dissolved calcium concentration.



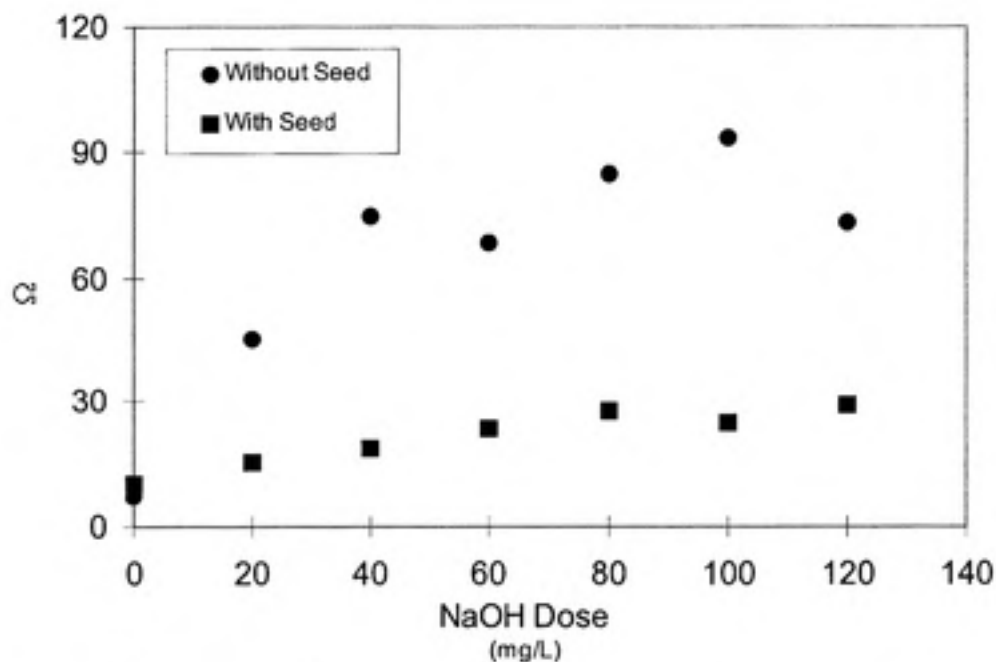
**Figure 4.20** Total calcium concentration resulting from softening with caustic soda with seed crystals (500 mg/L reagent-grade calcite) in the presence and absence of NOM (5 mg/L as C ). The solid line indicates the equilibrium model predictions for the dissolved calcium concentration.

The observed pH and calculated degree of saturation, with and without seed crystals in the presence of NOM, are presented in Figures 4.21 and 4.22, respectively. The pH observed when softening these waters in the presence of the seed crystals is lower than in the water without the seed crystals because there is more precipitation occurring in the former case. The supersaturation calculated for the water softened without any seed approaches values around 90, whereas the supersaturation of the waters softened in the presence of seed crystals is much lower.



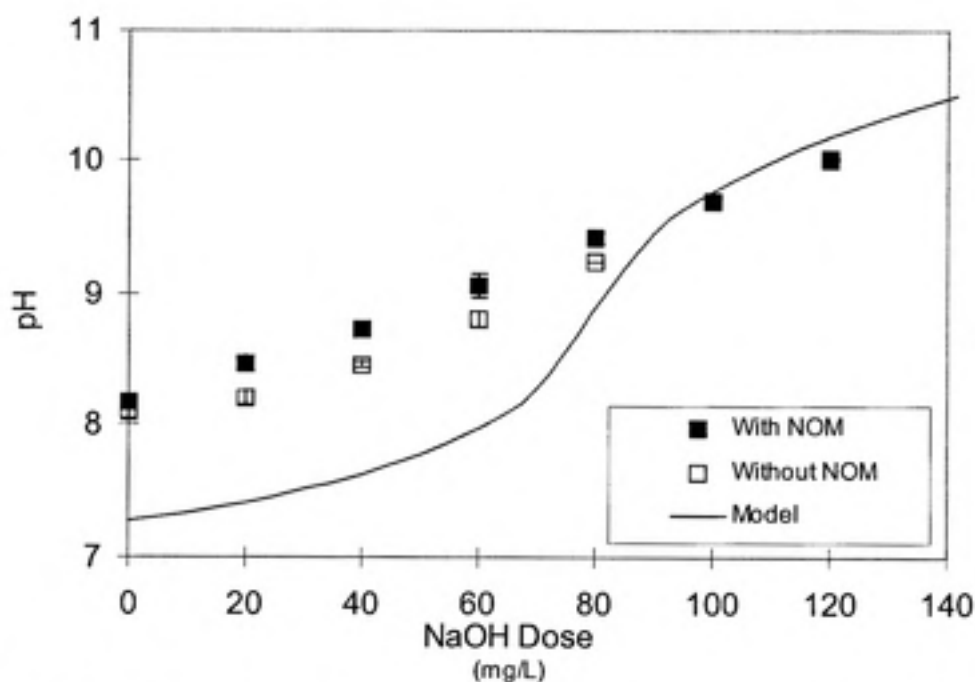
**Figure 4.21** pH resulting from softening with caustic soda in the presence of NOM (5 mg/L as C), with and without seed crystals (500 mg/L reagent-grade calcite). The solid line indicates the equilibrium model.



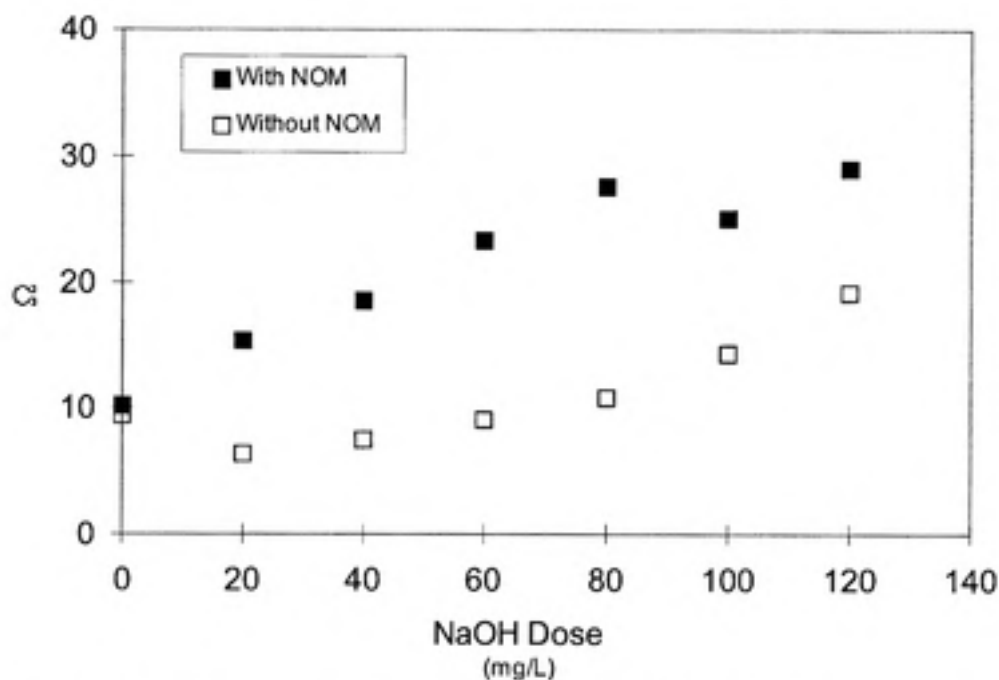


**Figure 4.22** Supersaturation resulting from softening with caustic soda in the presence of NOM (5 mg/L as C), with and without seed crystals (500 mg/L reagent-grade calcite).

Figures 4.23 and 4.24 present the observed pH and calculated degree of saturation for softened waters in the presence of seed crystals with and without NOM, respectively. The pH observed when softening water with NOM is higher than the water without NOM because there is less precipitation occurring. The supersaturation calculated for the water softened with NOM approaches values around 30, whereas the supersaturation of the waters softened in the absence of NOM is lower, indicating that more precipitation in the water with NOM would be expected, but was not observed.



**Figure 4.23** pH resulting from softening with caustic soda with seed crystals (500 mg/L reagent-grade calcite) in the presence and absence of NOM (5 mg/L as C). The solid line indicates the equilibrium model predictions.



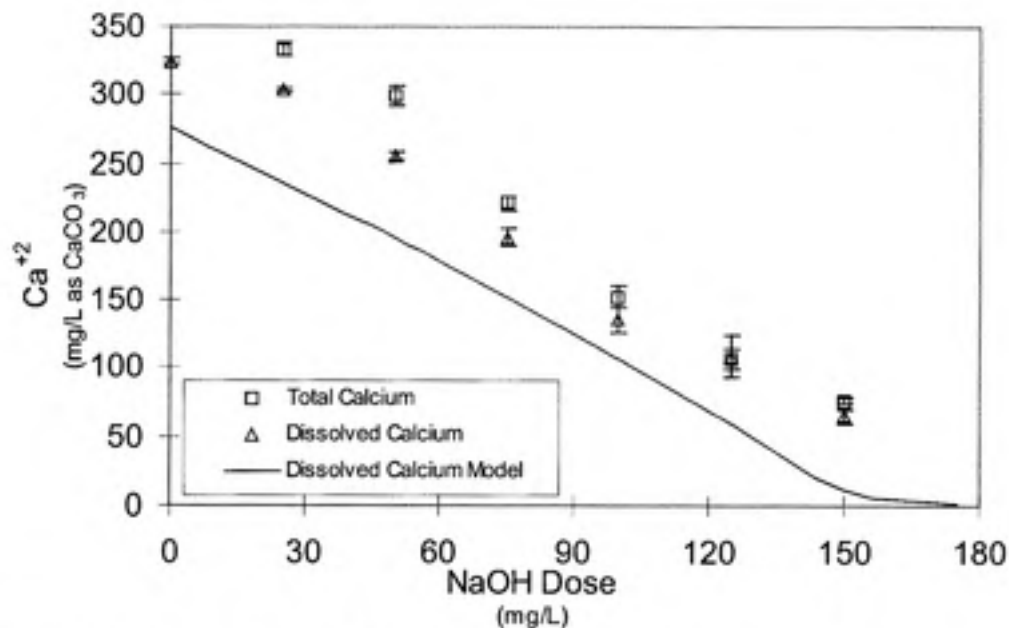
**Figure 4.24** Supersaturation resulting from softening with caustic soda (500 mg/L reagent-grade calcite) in the presence and absence of NOM (5 mg/L as C) with seed crystals.

#### **4.4 Softening Real Waters**

Two different raw drinking waters were softened with caustic soda, with and without seed crystals, to determine the benefits of seed crystal addition. These waters were first softened in the absence of seed crystals to determine an optimal dose of sodium hydroxide. Tests were then conducted with different amounts of seed to determine an optimal seed dose. Finally, the waters were softened again with increasing doses of caustic soda with the optimal dose of each of the seed crystals (reagent-grade calcite, Procter and Gamble seed, and dried sludge obtained from the respective water plants).

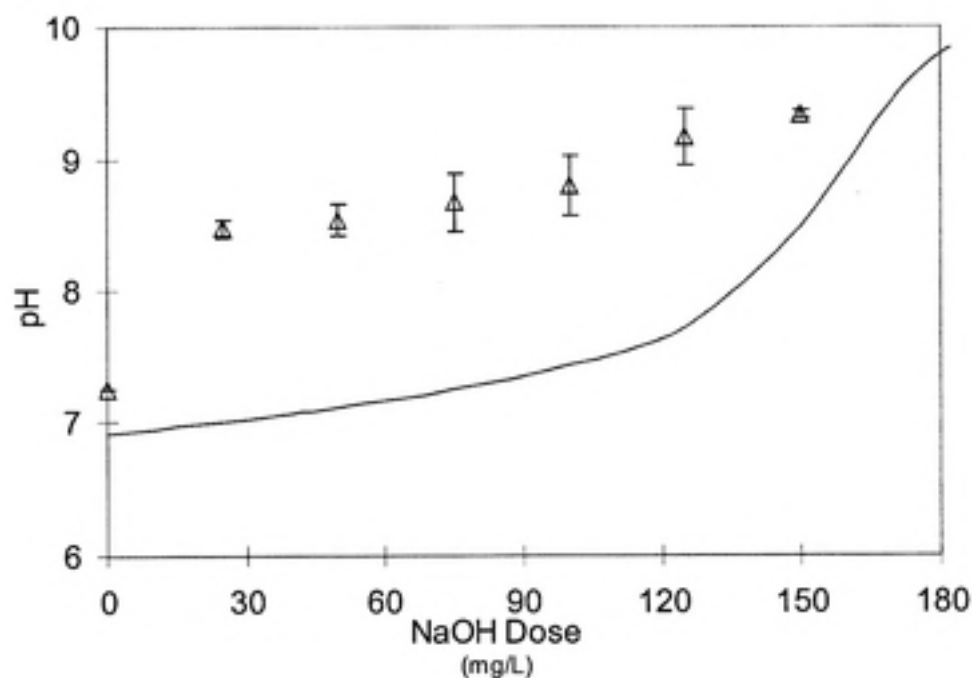
##### **4.4.1 Columbus, Ohio**

Raw water from Columbus, Ohio was obtained from the Parsons Water Treatment plant, whose source water comes from the Griggs and O'Shaugnessy Reservoirs. This water was chosen because it has high levels of total and calcium hardness and low levels of TOC. Figure 4.25 shows the results for the dissolved and total calcium concentrations obtained after softening with caustic soda in the absence of any seed crystals. It can be seen that at low doses of NaOH, the system is further from equilibrium, as predicted by the model, than at higher doses. Also, at higher NaOH doses, the dissolved and total calcium levels converge. This convergence is likely a result of more effective crystal formation due to the increased levels of supersaturation achieved at the higher NaOH doses.

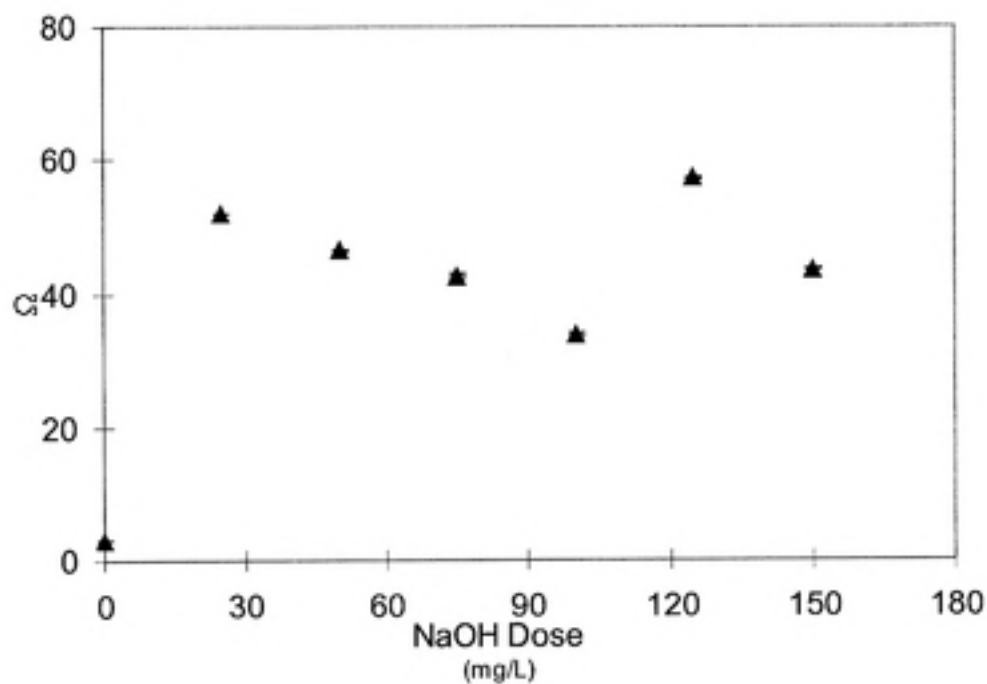


**Figure 4.25** Dissolved and total calcium concentrations resulting from precipitative softening of Ohio water with caustic soda (NaOH) without seed crystals. The solid line represents the equilibrium model predictions for the dissolved calcium concentration.

The corresponding pH and calculated levels of saturation are presented in Figures 4.26 and 4.27, respectively. The pH levels are not close to the values predicted by the equilibrium model, which indicates incomplete precipitation. These values, combined with the dissolved calcium concentrations presented in Figure 4.25 and the calculated  $C_T$  values, were used to calculate the degree of supersaturation. These values range from 30 to 60, confirming that precipitation is not effectively performed in the absence of a seeding agent.

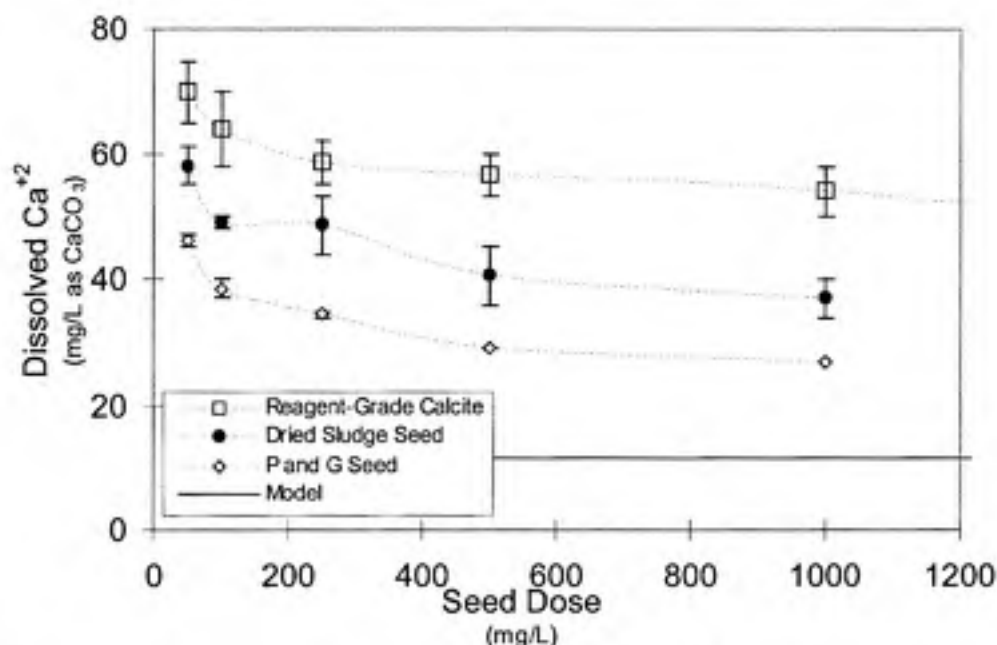


**Figure 4.26** pH resulting from precipitative softening of Ohio water with caustic soda (NaOH) without seed crystals. The solid line represents the equilibrium model predictions for the pH.



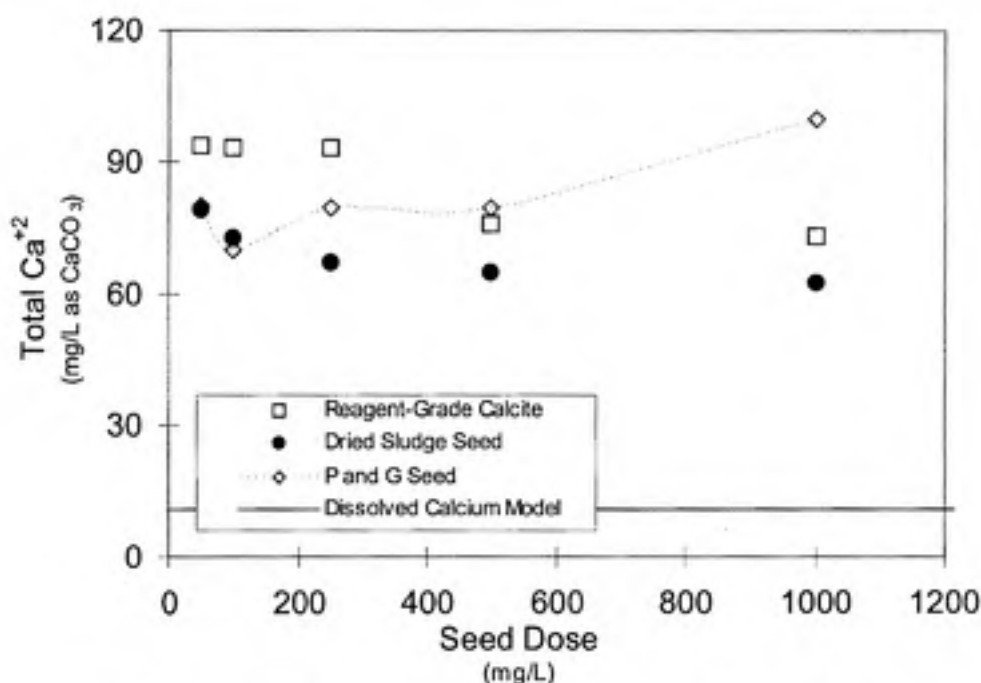
**Figure 4.27** Supersaturation resulting from precipitative softening of Ohio water with caustic soda (NaOH) without seed crystals.

The Ohio water was next softened with a NaOH dose of 150 mg/L and varying doses of the three seed crystals: reagent-grade calcite with a specific surface area of  $0.278 \text{ m}^2/\text{g}$ , the Procter and Gamble seed with a specific surface area of  $2.78 \text{ m}^2/\text{g}$ , and the dried sludge seed with a specific surface area of  $4.32 \text{ m}^2/\text{g}$ . These results are presented in Figures 4.28 and 4.29. Figure 4.28 shows that increasing the seed dose increases the removal of dissolved calcium in all cases. The Procter and Gamble seed appears to perform best over the range of NaOH doses tested despite the fact that the dried sludge has a higher specific surface area. However, the sludge seed is not pure calcium carbonate (approximately 80% calcite, 10% magnesium hydroxide), making it a less effective nucleating agent for  $\text{CaCO}_3$  crystallization than pure calcite.



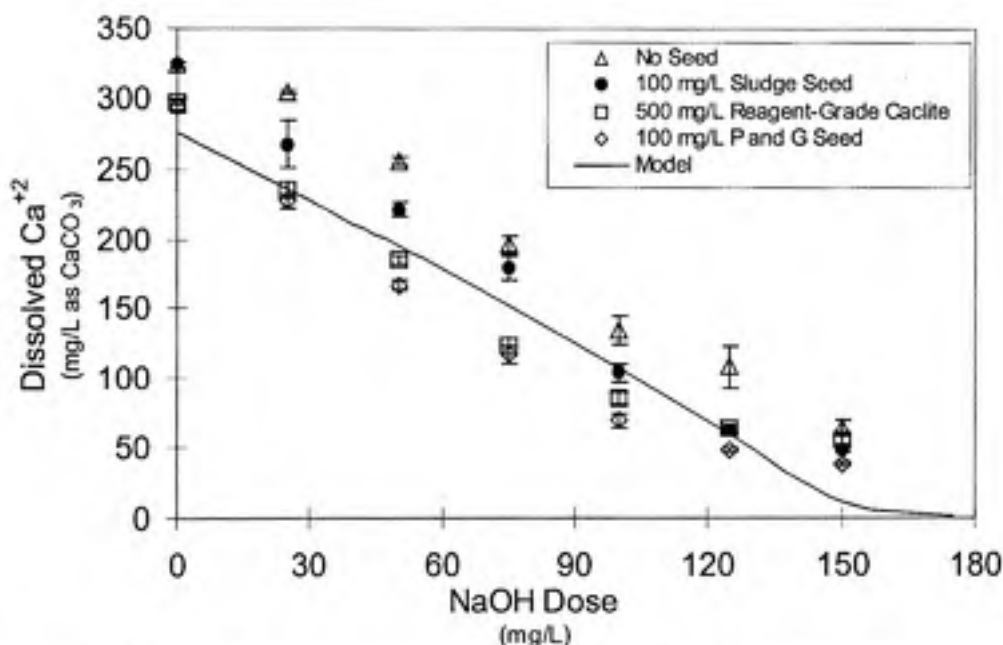
**Figure 4.28** Dissolved calcium concentrations resulting from precipitative softening of Ohio water with a constant NaOH dose (150 mg/L) and various seed crystal doses. The solid line shows the predicted dissolved calcium concentration in accordance with the equilibrium model.

Figure 4.29 shows that none of the seeding agents appreciably helped to reduce the total calcium concentrations. For the Procter and Gamble seed crystals, there is a slight improvement at 100 mg/L of seed, but at higher doses the total calcium concentration increases due to the fine nature of the Procter and Gamble seed, which results in ineffective settling. The other seed crystals give improved total calcium concentrations, but only to a limited degree. From these results and those presented in Figure 4.28, the optimum seed doses were chosen to be 100 mg/L for the Procter and Gamble seed, 500 mg/L for the reagent-grade calcite, and 100 mg/L for the dried sludge seed.



**Figure 4.29** Total calcium concentrations resulting from precipitative softening of Ohio water with a constant NaOH dose (150 mg/L) and various seed crystal doses. The solid line shows the predicted dissolved calcium concentration in accordance with the equilibrium model.

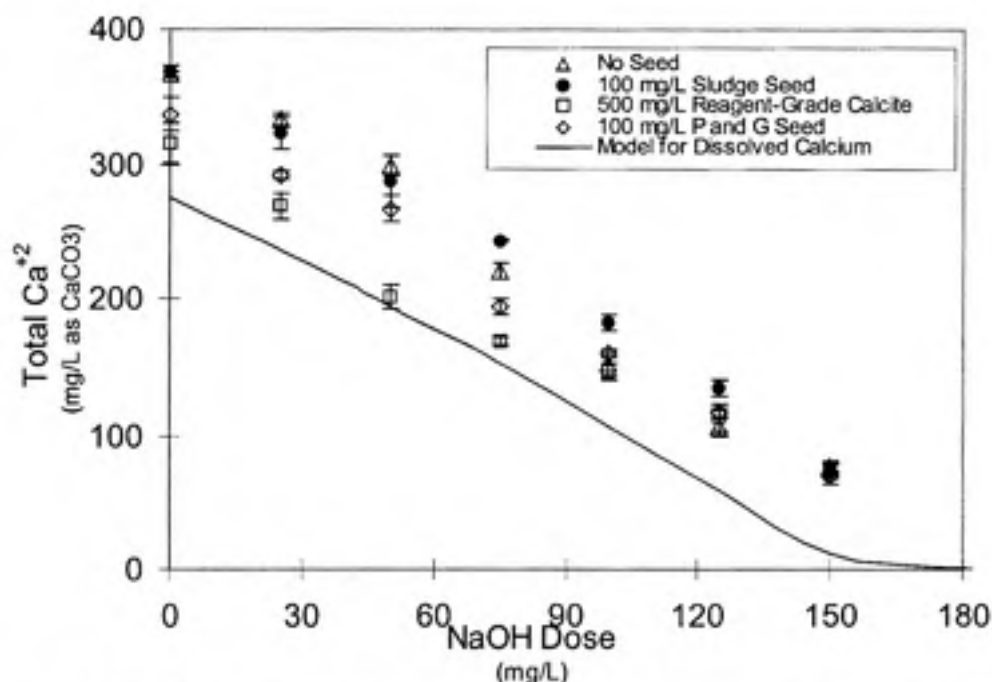
The Ohio water was softened with the optimal seed doses, and the results of these tests are presented in Figures 4.30-32. All seed crystals helped the dissolved calcium concentrations approach the values predicted by the equilibrium model. Figure 4.30 shows that the resulting dissolved calcium concentrations are lowest when the Procter and Gamble seed is used, followed by the reagent-grade calcite and dried sludge seed, in that order. At a dose of 150 mg/L NaOH, all the results seem to converge. At the seed doses that were used, it appears that the "clean" Procter and Gamble seed and reagent-grade calcite both did better than the dried sludge seed, which is comprised of  $\text{CaCO}_3$  with various impurities (e.g. magnesium hydroxide, NOM) which make it a less effective nucleating agent for  $\text{CaCO}_3$  precipitation than pure calcium carbonate.



**Figure 4.30** Dissolved calcium concentrations resulting from precipitative softening of Ohio water with caustic soda (NaOH) with and without seed crystals. The solid line represents the equilibrium model predictions.



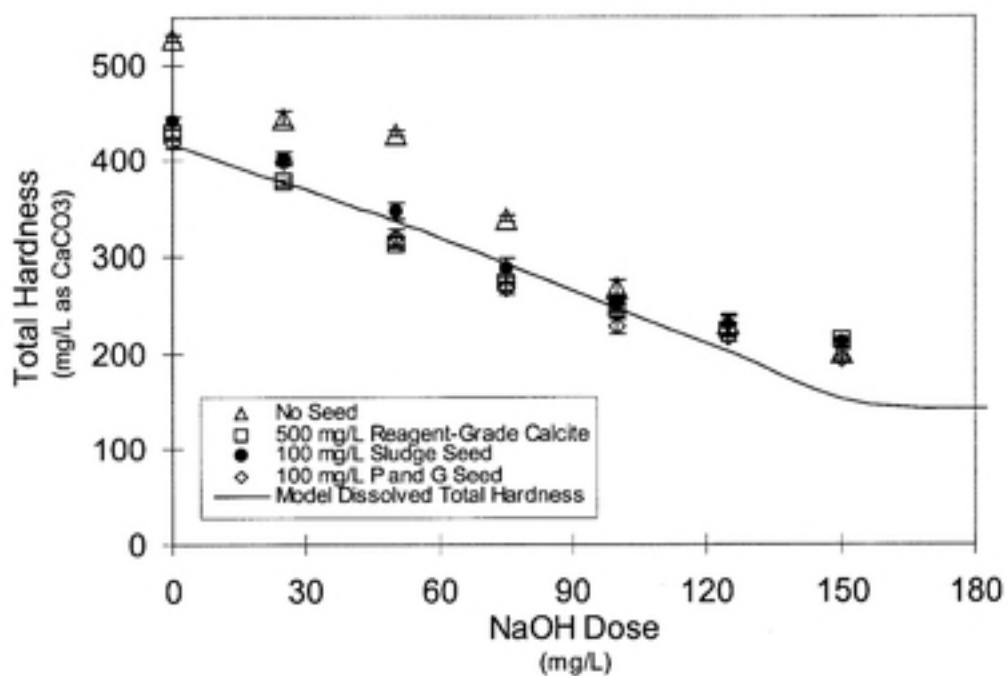
Figure 4.31 shows the results for the total calcium concentrations after softening in the presence of various seed crystals. The total calcium concentrations tended to be lower in the presence of seeds, except for the dried sludge seed, presumably because of its low particle size. The calcium concentrations were minimized when using the reagent-grade calcite, indicating that the precipitate formed during softening with this seed crystal settled most effectively. The total calcium remaining when using the Procter and Gamble seed crystals was greater than that found when using the reagent-grade calcite, again most likely because of the difference in the original crystal size.



**Figure 4.31** Total calcium concentration resulting from precipitative softening of Ohio water with caustic soda (NaOH) with and without seed crystals. The solid line represents the equilibrium model predictions for the dissolved calcium.

The total hardness resulting from precipitative softening with caustic soda is presented in Figure 4.32. These results are interesting when compared with the total calcium results presented in Figure 4.31. The total calcium concentrations were, for the most part, greater than the predictions for the equilibrium dissolved calcium concentrations, while the predictions for the total hardness at equilibrium were very close to the measured values. Total hardness is a measure of the dissolved calcium and magnesium concentrations remaining after softening, plus any solids, including precipitated calcium carbonate, magnesium hydroxide, or seed crystals, that did not settle in the time allowed.

The initial magnesium hardness of the Ohio water was 141 mg/L as  $\text{CaCO}_3$ , so its contribution to the effects of precipitation must be considered. It is not expected that much magnesium hydroxide precipitated since the measured pH was always less than 10 (the pH must be approximately 10.8 for magnesium hydroxide precipitation to occur), yet the magnesium concentration must have decreased significantly to make up for the excess calcium reported in Figure 4.31. The explanation for this could be a fault in the model, or it could be a result of adsorption reactions which are not accounted for in the model.

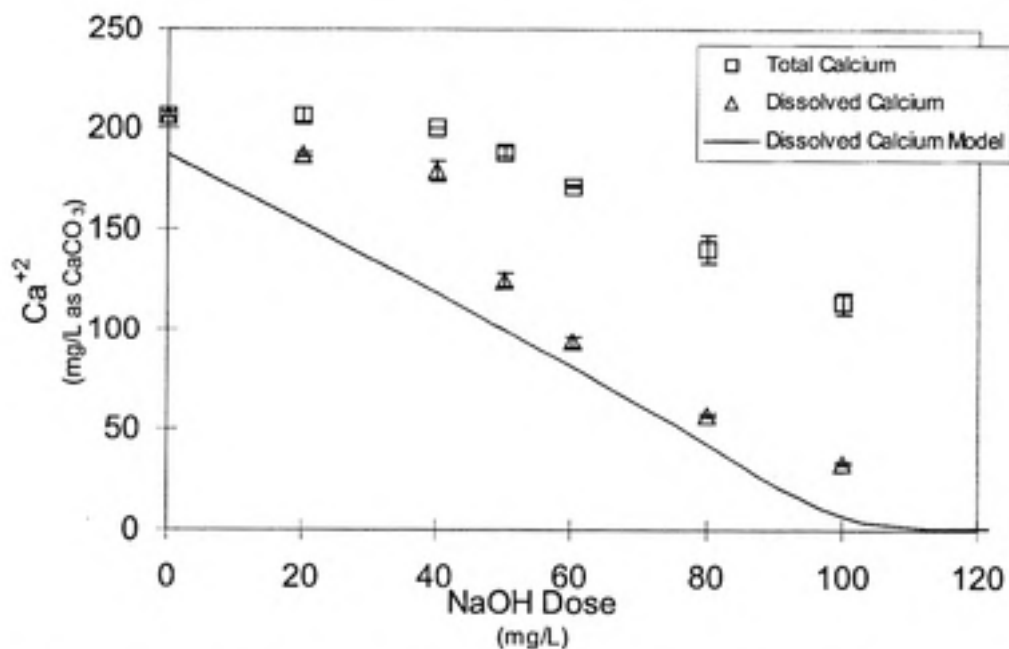


**Figure 4.32** Total hardness resulting from precipitative softening of Ohio water with caustic soda (NaOH) with and without seed crystals. The solid line represents the equilibrium model predictions for the dissolved total hardness.

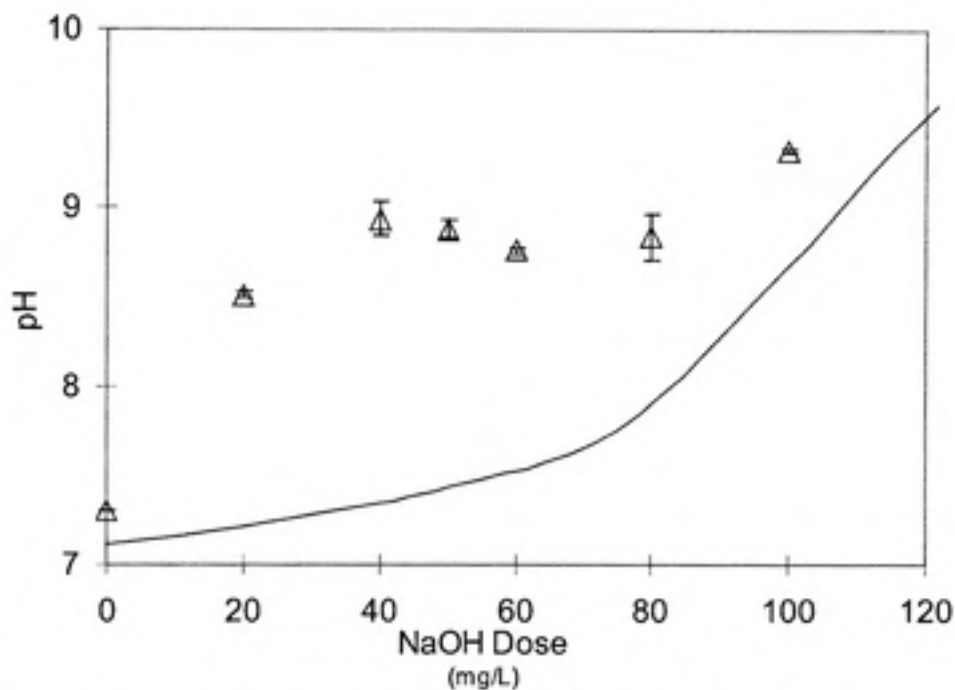
#### 4.4.2 Hialeah, Florida

Raw water from Miami, Florida was obtained from the Hialeah Water Treatment plant, whose source water comes from the Biscayne Aquifer. Figure 4.33 shows the results for the dissolved and total calcium concentrations obtained after softening with caustic soda in the absence of any seed crystals. It can be seen that the dissolved calcium concentrations do not follow the equilibrium predictions at low NaOH doses, but begin to approach the predicted values after a dose of 50 mg/L NaOH corresponding to a pH of 9. This behavior is similar to that observed for the experiments with the model water in the presence of NOM, and may be due to NOM binding dissolved calcium or blocking nucleation sites on the newly formed crystals until the phenolic groups become deprotonated at higher base doses in the vicinity of pH 9. The dissolved and total calcium concentrations do not converge as they did with the Ohio water. The total calcium concentrations remain appreciably higher than the corresponding dissolved calcium concentrations. This is most likely due to the presence of a high level of NOM which blocks nucleation sites and prevents the growth necessary to create crystals that will settle out of solution.

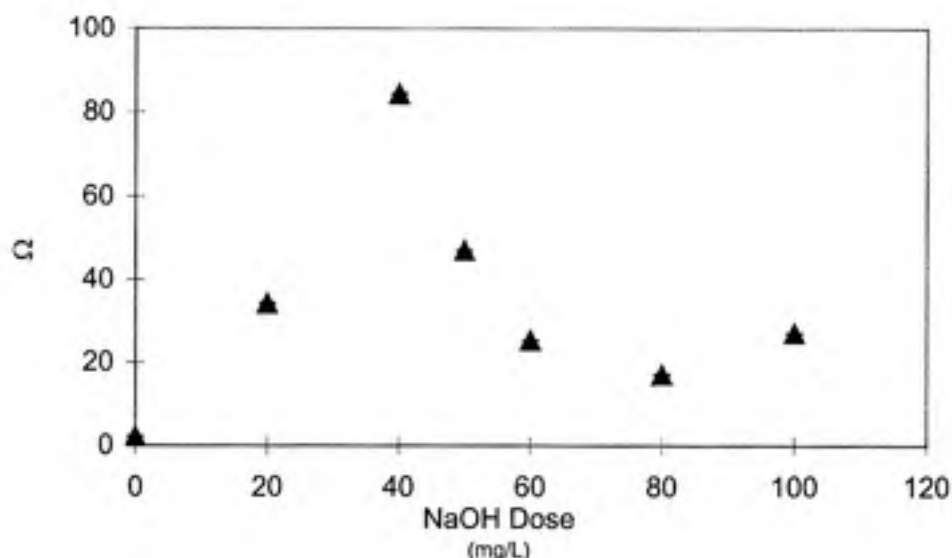
The pH and supersaturation for these tests is presented in Figures 4.34 and 4.35. It should be noted that the equilibrium model does not take into account the acid/base properties of NOM, i.e. it neglects the buffering effect of NOM. The measured pH demonstrates the buffering effect of the NOM in the region of 40 – 80 mg/L NaOH, around a pH of about 9. This is most likely a result of the deprotonation of the phenolic groups of the NOM, which begins to occur at a pH of 9. The calculated supersaturations included in Figure 4.32 increase dramatically before until pH 9, after which it decreases due to more effective  $\text{CaCO}_3$  precipitation in accordance with the equilibrium model.



**Figure 4.33** Dissolved and total calcium concentration resulting from precipitative softening of Florida water with caustic soda (NaOH) without seed crystals. The solid line represents the equilibrium model predictions for the dissolved calcium concentration.

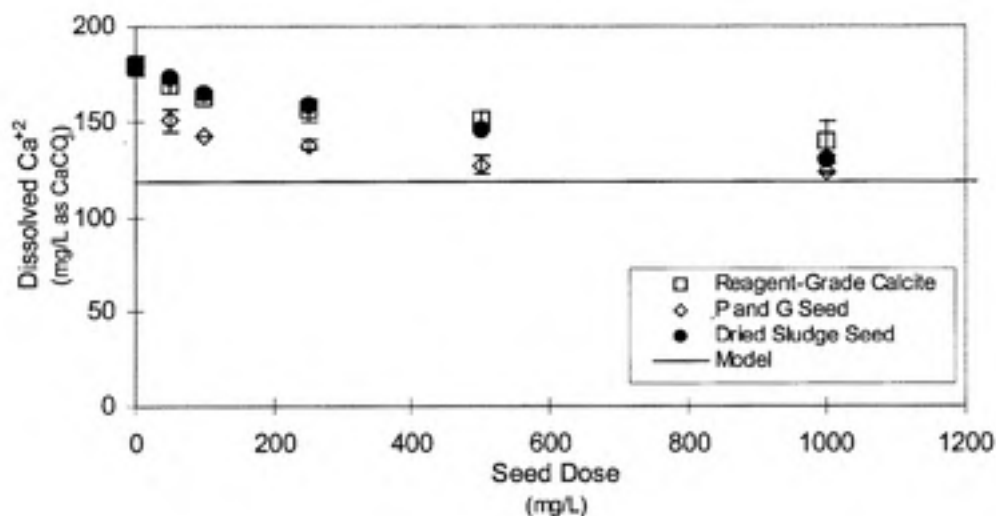


**Figure 4.34** pH resulting from precipitative softening of Florida water with caustic soda (NaOH) without seed crystals. The solid line represents the equilibrium model predictions for the pH.

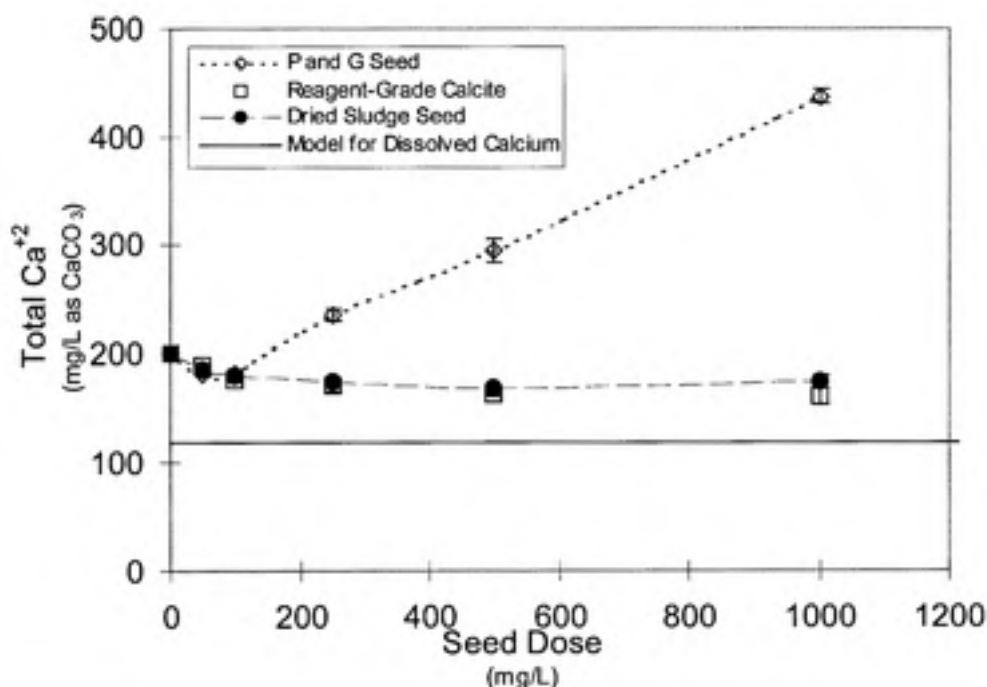


**Figure 4.35** Supersaturation resulting from precipitative softening of Florida water with caustic soda (NaOH) without seed crystals.

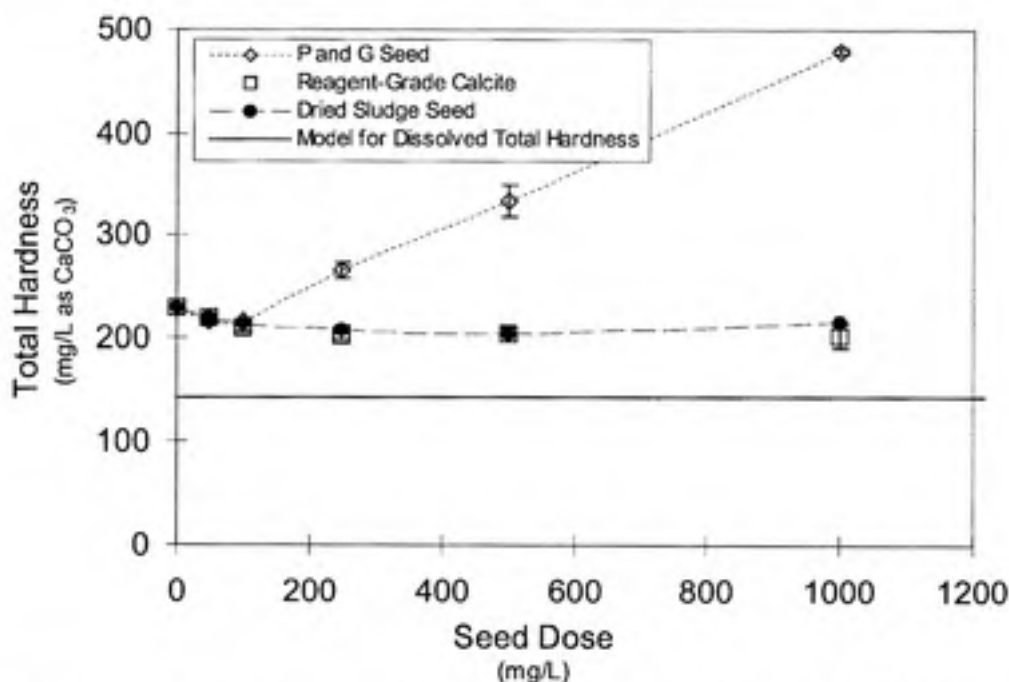
The Florida water was softened with a NaOH dose of 40 mg/L and varying doses of three seed crystals; in addition to the reagent-grade calcite and the Procter and Gamble seed crystals, dried sludge solids from the Hialeah Water Treatment Plant were used. These results are presented in Figures 4.36-38. Figure 4.36 shows that increasing seed doses increase the removal of dissolved calcium in all cases. The results for the Procter and Gamble seed crystals appear to approach equilibrium dissolved calcium concentrations at lower seed crystal doses than the others, most likely because it presents the cleanest and greatest surface area. However, the results for the total calcium concentration shown in Figure 4.37 and the total hardness concentration shown in Figure 4.38 demonstrates that at higher seed doses the Procter and Gamble seed crystals do not settle effectively from solution, leading to total calcium and total hardness levels in excess of those of the original hard water. The reagent-grade calcite and dried sludge solids performed almost identically.



**Figure 4.36** Dissolved calcium concentration resulting from precipitative softening of Florida water with 40 mg/L NaOH and various seed crystal doses. The model predictions for the dissolved calcium concentration are represented by the solid line.



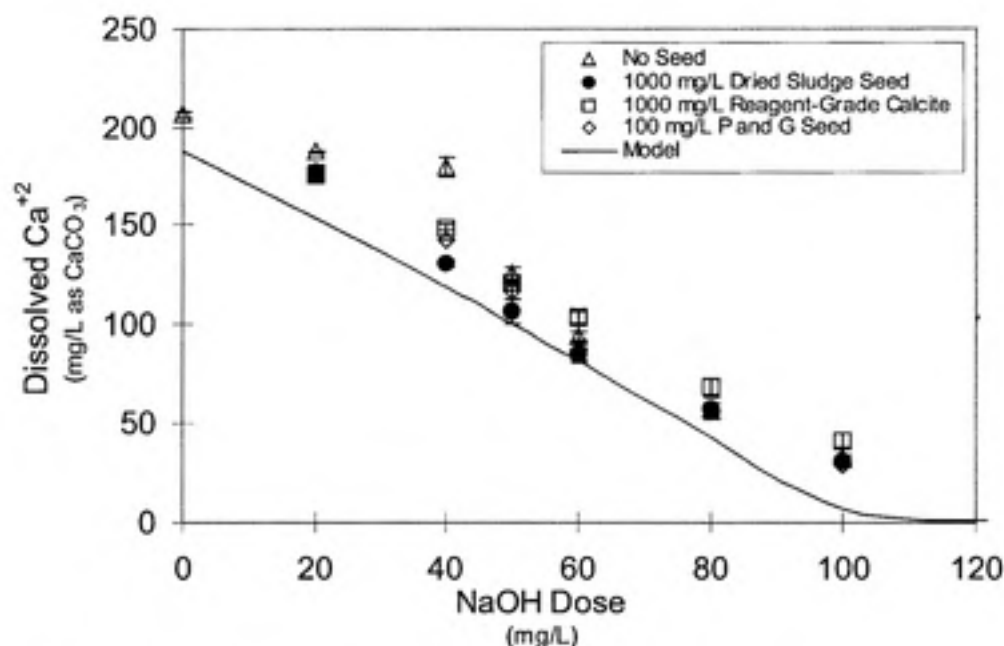
**Figure 4.37** Total calcium concentration resulting from precipitative softening of Florida water with 40 mg/L NaOH and various seed crystal doses. The model predictions for the dissolved calcium concentration are represented by the solid line.



**Figure 4.38** Total hardness resulting from precipitative softening of Florida water with 40 mg/L NaOH and various seed crystal doses. The solid line shows the predicted dissolved total hardness concentration.

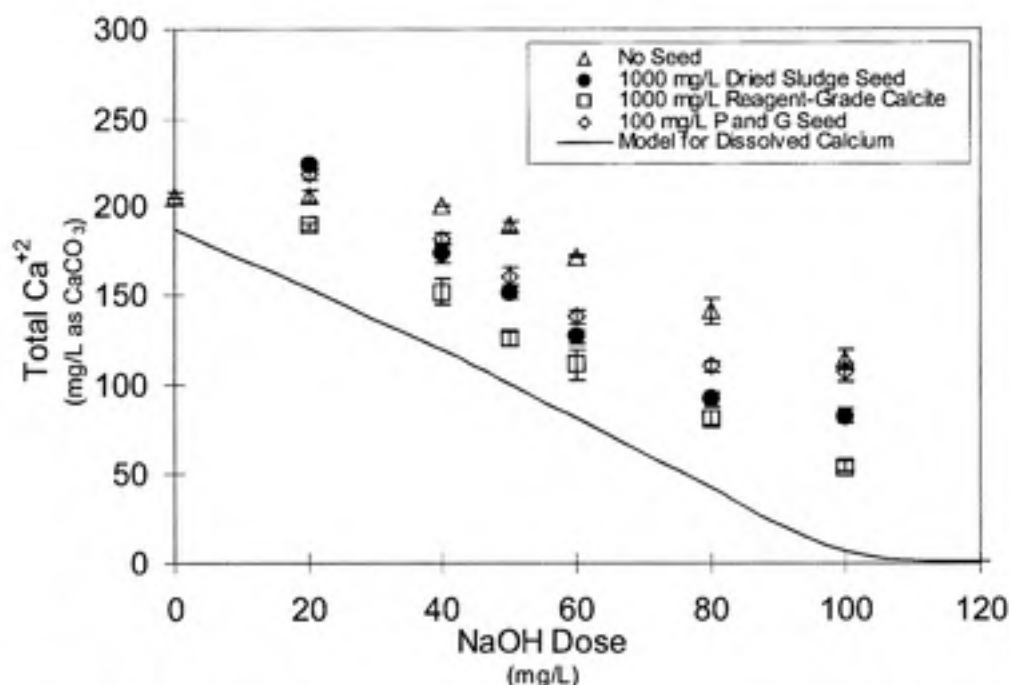
Based on the results of the seed dose tests, the optimal seed doses were chosen to be 100 mg/L for the Procter and Gamble seed, 1000 mg/L for the reagent-grade calcite, and 1000 mg/L for the dried sludge seed. The Florida water was softened with these seed doses, and the results of these tests are presented in Figures 4.39-41. Figure 4.39 shows that the seed crystals help to lower the final dissolved calcium concentration for NaOH doses up to 50 mg/L (pH 8.6 – 8.7). Thereafter, the results with the seed crystals were approximately the same as the unseeded solutions. It appears that the NOM in this high TOC water does not impact the effectiveness of the seed crystals in helping the dissolved calcium concentrations approach the predictions of the equilibrium model.



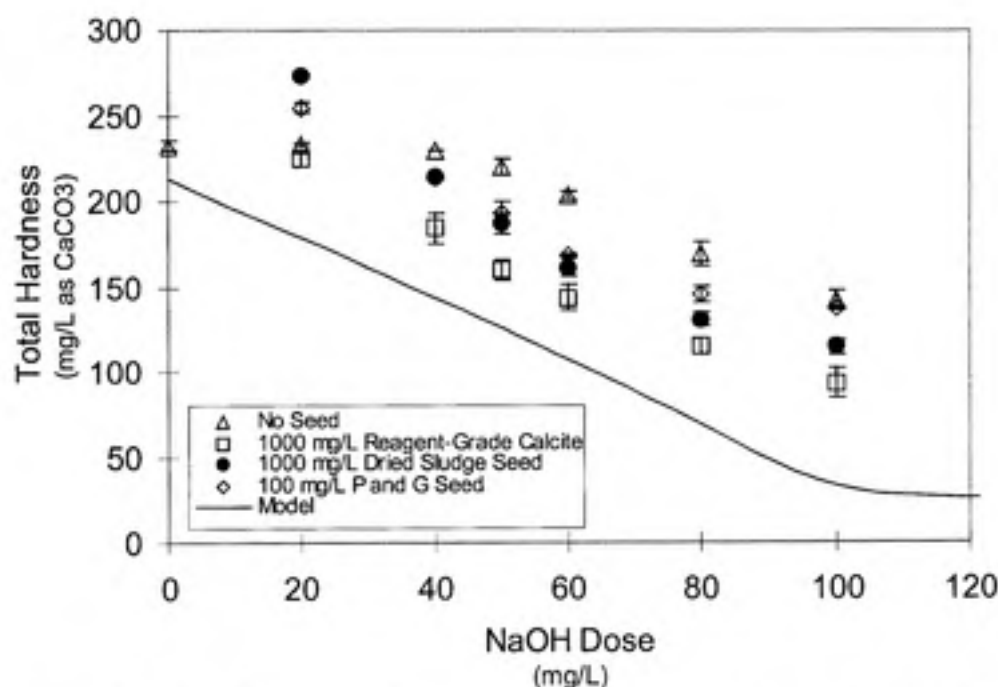


**Figure 4.39** Dissolved calcium concentration resulting from precipitative softening of Florida water with caustic soda (NaOH) with and without seed crystals. The solid line represents the equilibrium model predictions for the dissolved calcium concentration.

Figures 4.40 and 4.41 show the results for the total calcium concentration and total hardness, respectively. The results indicate that both are reduced when using these three crystal seeds. The precipitate formed during softening with the larger reagent-grade crystals appear to settle most effectively. The precipitate formed with the Procter and Gamble seed crystals settle least effectively, most likely due to the finer nature of these crystals.



**Figure 4.40** Total calcium concentration resulting from precipitative softening of Florida water with caustic soda (NaOH) with and without seed crystals. The solid line represents the equilibrium model predictions for the dissolved calcium concentration.



**Figure 4.41** Total hardness resulting from precipitative softening of Florida water with caustic soda (NaOH) with and without seed crystals. The solid line represents the equilibrium model predictions for the dissolved total hardness concentration.

## CHAPTER 5: CONCLUSIONS

The results of this study demonstrate that addition of the Procter and Gamble seed crystals improved the removal of dissolved calcium during precipitative softening with caustic soda. The optimal seed dose of the Procter and Gamble seed crystals was found to be approximately ten times lower than that for reagent-grade calcium carbonate, primarily because the specific surface area of the Procter and Gamble seed was about ten times greater than that of the reagent-grade calcite. For doses of equal surface area, there was no significant difference between the performances of the Procter and Gamble seed and the reagent-grade calcite in removing calcium hardness.

In tests with two real waters, the presence of seed crystals increased the precipitation of calcium carbonate when softening with caustic soda. Higher doses of seed crystals increased the precipitation of calcium carbonate until the equilibrium condition was approached. However, higher doses of the Procter and Gamble seed crystals caused the total calcium concentration to increase. This is believed to be due to the fine nature of these seed crystals, which did not readily settle from solution. The presence of a high level of NOM in Florida ground water did not significantly affect the removal of calcium hardness through heterogeneous nucleation.

The results of this study showed that the effect of seed crystal addition during lime softening is negligible for improving dissolved calcium carbonate precipitation. This is due primarily to the fact that when lime is added to water, it is first slaked to become  $\text{Ca(OH)}_2$  or "milk of lime", resulting in a slurry that provides a surface for

calcium carbonate crystal growth and eliminating the need for additional nucleating agents. However, the addition of reagent-grade calcite seed crystals in the softening of a synthetic hard water did improve total calcium removal by aiding in the settling of the solid precipitate.

NOM appeared to inhibit the precipitation and removal of calcium from synthetic hard water during heterogeneous nucleation. This inhibition was most likely the result of adsorption of NOM to the surface of the calcium carbonate precipitate, which inhibited crystal growth. The effects of NOM were found to be pH-dependant. At pH values below 9, NOM was found to be more inhibitory than at pH values greater than 9. This is attributed to deprotonation of the phenolic groups of the NOM which cause it to exhibit different properties. These effects were more pronounced during homogenous nucleation. The presence of seed crystals employed in heterogeneous nucleation tended to counteract the inhibitory effects of NOM which appeared to be blocking the homogenous nucleation sites.

A possible avenue of future investigation might be to explore the effects of using a coagulant with the Procter and Gamble crystal seed. If the fine calcium carbonate crystals that are formed when using the Procter and Gamble seed crystals could be aggregated, this might improve their settling characteristics. Adding a coagulant prior to sedimentation should be examined.

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**APPENDIX A:**  
**Modeling Precipitative Softening**



1. Raw Water Characteristics

$$\text{Alkalinity (Alk}_o\text{)} = 270 \text{ mg/L as CaCO}_3 = 0.0054 \text{ eq/L}$$

$$\text{pH} = 7.3$$

$$\text{Total Hardness (TH}_o\text{)} = 465 \text{ mg/L as CaCO}_3 = \text{CH} + \text{MH} = 0.00465 \text{ M}$$

$$\text{Calcium Hardness} = 324 \text{ mg/L as CaCO}_3 = 0.00324 \text{ M}$$

$$\text{Magnesium Hardness} = 141 \text{ mg/L as CaCO}_3 = 0.00141 \text{ M}$$

2. Calculate Alpha Fractions for Carbonate System

$$\alpha_0 = \frac{[\text{H}_2\text{CO}_3^*]}{C_T} = \frac{1}{1 + K_1/[\text{H}^+] + K_1K_2/[\text{H}^+]^2} = 0.1008$$

$$\alpha_1 = \frac{[\text{HCO}_3^-]}{C_T} = \frac{1}{[\text{H}^+]/K_1 + 1 + K_2/[\text{H}^+]} = 0.8984$$

$$\alpha_2 = \frac{[\text{CO}_3^{2-}]}{C_T} = \frac{1}{[\text{H}^+]^2/(K_1K_2) + [\text{H}^+]/K_2 + 1} = 0.0008$$

2. Calculate  $C_{T0}$

$$C_{T0} = \frac{\text{Alk}_o - [\text{OH}^-] + [\text{H}^+]}{\alpha_1 + 2\alpha_2} = 0.006 \text{ M}$$

4. Calculate  $(C_B - C_A)_0$

$$(C_B - C_A)_0 = C_{T0}(\alpha_1 + 2\alpha_2) + [\text{OH}^-] - 2[\text{Ca}^{+2}] - 2[\text{Mg}^{+2}] - [\text{H}^+] = -0.0039 \text{ eq/L}$$

5. Initial Parameters – For any NaOH dose:

$$C_{T0}^* = \text{constant} \quad [\text{Ca}^{+2}]^* = \text{constant} \quad [\text{Mg}^{+2}]^* = \text{constant}$$

For the addition of 100 mg/L NaOH (0.0025 M):

$$(C_B - C_A)_0^* = (C_B - C_A)_0 + [\text{Na}^+] = -0.0014 \text{ eq/L}$$

6. Quadratic to solve for the amount of  $\text{CaCO}_3$  precipitated ( $P_{\text{CaCO}_3}$ ) w/ initial pH

$$(P_{\text{CaCO}_3})^2 + P_{\text{CaCO}_3}(-[\text{Ca}^{+2}]_0^* - C_{\text{T}0}^*) + \left[ [\text{Ca}^{+2}]_0^* [C_{\text{T}}]_0^* - \frac{K_{\text{so,CaCO}_3}}{\alpha_2} \right] = 0$$

$$\text{where } a = 1, b = (-[\text{Ca}^{+2}]_0^* - C_{\text{T}0}^*), c = \left[ [\text{Ca}^{+2}]_0^* [C_{\text{T}}]_0^* - \frac{K_{\text{so,CaCO}_3}}{\alpha_2} \right]$$

If  $P_{\text{CaCO}_3} < 0$ , then  $P_{\text{CaCO}_3} = 0$ , else  $P_{\text{CaCO}_3} = P_{\text{CaCO}_3}$ .

7. Solve for the amount of  $\text{Mg}(\text{OH})_2$  precipitated ( $P_{\text{Mg}(\text{OH})_2}$ ) w/ initial pH.

$$P_{\text{Mg}(\text{OH})_2} = [\text{Mg}^{+2}]_0^* - K_{\text{so,Mg}(\text{OH})_2} \left[ \frac{K_w}{[\text{H}^+]} \right]^{-2}$$

If  $P_{\text{Mg}(\text{OH})_2} < 0$ , then  $P_{\text{Mg}(\text{OH})_2} = 0$

Steps 6 and 7 are linked to the pH through  $[\text{H}^+]$ , so they must be solved in conjunction with the charge balance.

8. Solve for pH through charge balance

$$[\text{Ca}^{+2}] = ([\text{Ca}^{+2}]_0^* - P_{\text{CaCO}_3})$$

$$[\text{Mg}^{+2}] = ([\text{Mg}^{+2}]_0^* - P_{\text{Mg}(\text{OH})_2})$$

$$C_{\text{T}} = [C_{\text{T}}]_0^* - P_{\text{CaCO}_3}$$

$$2[\text{Ca}^{+2}] + 2[\text{Mg}^{+2}] + [\text{H}^+] + (C_{\text{B}} - C_{\text{A}}) - C_{\text{T}}(\alpha_1 + 2\alpha_2) - [\text{OH}^-] = 0$$

The only unknown here is  $[\text{H}^+]$ . This equation can be solved using the Goal Seek function in Microsoft EXCEL by setting it equal to zero and changing the pH. By linking 6 and 7 to this equation, EXCEL will continuously update until all equations are solved.

For this case, the final pH = 7.42,  $[\text{Ca}^{+2}] = 0.00107 \text{ M}$ ,  $P_{\text{CaCO}_3} = 0.0022 \text{ M}$ , no Mg precipitation.